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## ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## PART II.

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## General and Physical Chemistry.

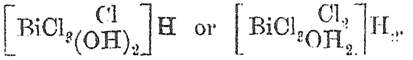
**Optical Researches on the Constitution of Bismuth Compounds.** KONR. SCHÄFER and FR. HEIN (*Zeitsch. anorg. Chem.*, 1917, **100**, 249—303).—Optical differences between ions and undissociated molecules may be due to a change in the composition of the chromophore through dissociation, or more probably to the fact that the absorption spectrum is dependent on the degree of solvation of the chromophoric cation. The dissociation of a salt $KA$ with a coloured cation may be represented by the scheme:

$$KA \longrightarrow \begin{bmatrix} A \\ K(OH_2)_n \end{bmatrix} \longrightarrow [K(OH_2)_n]A \longrightarrow [K(OH_2)_n]^{\cdot} + A'.$$

The degree of completion of dissociation at any dilution depends on the relative strengths of the affinities $K \longleftrightarrow A$ and $K \longleftrightarrow$ solvent, and the solution may come to a condition of optical equilibrium before complete dissociation. If the force $K \longleftrightarrow A$ is strong, dissociation is incomplete and the anion remains combined with the chromophoric complex. This condition of affairs probably obtains in the case of the bismuth haloids.

Solutions of bismuth chloride in aqueous hydrochloric acid show a deep absorption band having its apex at $1/\lambda = 3070$. Since the depth and persistence of the band are both increased by increasing the concentration of the acid, it is probable that there is formed in solution a complex bismuthchlorhydric acid. In weaker acid solutions, although the depth of the absorption band is less than with stronger acid, the intensity in the neighbourhood of the band minimum is much greater. This is taken as evidence of the formation of bismuthyl complexes in such solutions. Proof of this is furnished by the observation that weakly acid solutions of bismuth chloride in equilibrium with solid bismuth oxychloride show an even greater intensity at the minimum point with an increase in the width of the band. The absorption curves of bismuth chloride in ammonium chloride solutions are practically the same as in hydrochloric acid solutions.

Solutions of bismuth chloride in dry ether or ethyl acetate give probably the true absorption band of the salt itself. The band is farther in the ultra-violet than in hydrochloric acid solutions, having its maximum near $1/\lambda = 3400$, and is shallower. Addition of hydrochloric acid and a very small quantity of water to the ethereal solution, however, shifts the band back to the same position as in the aqueous acid solutions. The remarkable effect of the water makes it seem probable that the absorbing complexes are of the type



$$\left[\mathrm{BiCl_3}\overset{\mathrm{Cl}}{\underset{(\mathrm{OH})_2}{}}\right]\mathrm{H} \text{ or } \left[\mathrm{BiCl_3}\overset{\mathrm{Cl_2}}{\underset{\mathrm{OH_2}}{}}\right]\mathrm{H_2}.$$

By leading dry hydrogen chloride into an ethereal solution of bismuth chloride, a new compound, $BiCl_3,HCl,2OEt_2$, was isolated, in the form of a colourless, viscous oil.

Bismuth bromide in aqueous hydrobromic acid is similar to bismuth chloride, the absorption band being shifted into the visible spectrum with its maximum near $1/\lambda = 2700$. In ether, the band is shifted towards the violet, and there is only a suggestion of selective absorption. Addition of hydrogen bromide to the ether solution, however, immediately brings the band back to $1/\lambda = 2700$, without the addition of water. The inference is that the absorbing complex is a simple bismuthbromhydric acid.

Two new compounds of bismuth bromide were isolated in the form of unstable hygroscopic powders, their compositions being $H_2BiBr_5,4OEt_2$ and $H_2BiBr_5,10OEt_2$.

Bismuthyl compounds, such as potassium tribismuthyl tartrate and compounds with glycerol and mannitol, show only general absorption in the region of the bismuth chloride band in ether. Bismuth nitrate, sulphate, and perchlorate in aqueous solutions of their respective acids show slight general absorption in the ultra-violet. The conclusion is drawn that, since bismuth ions and bismuthyl compounds show no absorption bands, the bismuth haloids must be classed with abnormal salts of the type of mercuric cyanide.

Bismuth trimethyl in alcohol, bismuth triphenyl in ether, and bismuth triphenyl dichloride in chloroform all show fairly strong general absorption in the ultra-violet. For the preparation of bismuth trimethyl, a new method was devised, using Grignard's reagent. E. H. R.

**The Influence of Solvents on the Absorption of Light by Dissolved Substances.** A. Hantzsch (*Ber.*, 1917, **50**, 1413—1421). —From earlier investigations, it is probable that the accuracy of the optical absorption method for the examination of keto-enol equilibria with ethyl acetoacetate and similar substances is not seriously influenced by the formation of additive compounds between solute and solvent. Evidence to this effect is also supplied by the behaviour of the structurally simple trinitrotriphenylcarbinol, which exhibits almost identical absorption curves in methyl alcohol and in chloroform, although with these substances it forms isolable additive compounds, $OH\cdot C(C_6H_4\cdot NO_2)_3,CH_3OH$ and $OH\cdot C(C_6H_4\cdot NO_2)_3,CHCl_3$ respectively. The character of the absorption by trinitrotriphenylcarbinol, and presumably by all substances of definite and fixed constitution, is therefore not appreciably affected by combination with the solvent. The fact that acetic acid in the pure condition and in concentrated aqueous solution possesses identical absorptive properties for light (Hantzsch, A., 1914, ii, 5) proves that mere hydration also is without optical effect, and even association into the bimolecular condition, as experienced with acetic acid and with trichloroacetic acid, has no marked influence in this direction; a parallelism is suggested between the formation of such unstable molecular compounds in which the combined molecules are alike and unlike, the processes being described respectively as homogeneous and heterogeneous association. Heterogeneous association with an optically transparent medium is generally accompanied by a slight change in the absorption curve of the solute, but the general nature of the absorption remains unaltered. As very few substances can be regarded as completely saturated, slight changes in the absorption spectrum may be met frequently. In contrast with such cases stands the behaviour of substances which in different solvents show essentially diverse absorption, due to definite constitutional modification, the extent of which is influenced by the solvent; tautomeric substances present the best known examples of this class. In considerations such as these, care is necessary to avoid confusion with cases in which chemical reaction occurs between solvent and solute, with the formation of new substances possessing absorptive properties different from those of the solute; the medium is then better described as a pseudo-solvent. Chloral and alloxan dissolved in water undergo loss of the ketonic oxygen with replacement by two hydroxyl groups, and this definite structural change produces a corresponding marked alteration in the absorption spectrum of each. From the point of view now under consideration, genuine solvents either give rise to no marked "solvate" formation or form unstable and feeble heterogeneous association products involving only trivial chemical and optical alteration; they may, however, by affecting the stability of the solvates, influence the equilibrium between the stable and metastable forms of a tautomeric substance, and thereby produce material alteration in the chemical constitution and optical properties. It is necessary to remember the possibility that a liquid may act concurrently in two different ways, partly as a genuine solvent and partly as a pseudo-solvent with chemical action, thus giving rise to an equilibrium between solvates and chemical compounds. D. F. T.

**The Constitution of Carboxylic Acids and the Optical and Chemical Processes in the Formation of Esters, Salts, and Ions.** A. Hantzsch (*Ber.*, 1917, **50**, 1422—1457. Compare preceding abstract).—The ordinary structural formula $R\cdot CO\cdot OH$ for the carboxylic acids is insufficient for many purposes, and fails, for example, to explain satisfactorily the relative ease with which the hydrogen of the hydroxyl group undergoes scission by electrolytic dissociation. The optical absorptive characteristics of the organic acids and their derivatives also demand an improved method for formulating the structure of the acids; thus the salts of a fatty acid with the alkali or alkaline earth metals are optically identical with one another, as also are the alkyl esters, but the esters always exhibit a more marked absorption than the salts, whilst the free acids commonly occupy an intermediate position, although in extreme cases they may become optically identical with the salts or with the esters; these optical differences can be due only to chemical, and therefore to constitutive, differences, because chemically and optically indifferent solvents have only a negligible effect on the absorption spectrum of the solute (see preceding abstract), association of a fatty acid, for example, acetic acid, does not affect the absorption, electrolytic dissociation is without influence on the optical absorption by fatty acids, and the mere replacement of the hydrogen of an acid by an alkyl radicle leaves the absorption spectrum practically unchanged. Investigation of trichloroacetic acid demonstrates that in solution in water or light petroleum the acid possesses optical properties coincident with those of aqueous solutions of the salts, but that in alcohol or ether the absorption by the acid is identical with that of solutions of the esters in alcohol, ether, or light petroleum, the two absorption curves being quite distinct; this difference cannot be explained by assuming the formation of an acid ortho-ester in alcoholic solutions of the acid, because ortho-esters, being more saturated, should possess more feeble absorptive powers, whereas the alcoholic solutions of trichloroacetic acid give the absorption band nearer the visible spectrum. The conclusion is therefore drawn that whilst the alkyl groups in the alkyl esters are attached to an oxygen atom in the usually accepted manner, the ionisable atoms are attached to both oxygen atoms, the structure of the salts and acid being representable by the formulæ $CCl_3\cdot C{<}\begin{smallmatrix}O\\O\end{smallmatrix}\Big\}M$ and $CCl_3\cdot C{<}\begin{smallmatrix}O\\O\end{smallmatrix}\Big\}H$ respectively, these constitutions being analogous to Werner's method of expressing the ionisability of inorganic salts by "ionogenic" linkings; the formula $R\cdot CO\cdot OH$ therefore is that of a *pseudo*-acid corresponding with a true acid of the structure $R\cdot C{<}\begin{smallmatrix}O\\O\end{smallmatrix}\Big\}H$. Although trichloroacetic acid from its absorption spectrum appears to be of the former constitution in alcoholic or ethereal solution, and of the latter constitution in water or light petroleum, the phenomenon is in reality one of equilibrium, and by more sensitive methods of examination, for example, by means of the electrical conductivity, it is possible to detect the presence of a definite, although small, proportion of the true acid modification in the alcoholic solution. The behaviour of other carboxylic acids is of the same general character as that of trichloroacetic acid, but somewhat less simple, solutions in alcohol or ether containing the acid almost entirely in the pseudo-modification, whilst the acid in the free state or when dissolved in light petroleum or water consists of a mixture of the pseudo- and true acid modifications in equilibrium. In this case, the relation between the esters, the free acid, and the salts may be represented by the scheme: $R\cdot CO\cdot O\cdot C_nH_{2n+1},R\cdot CO\cdot OH \rightleftharpoons R\cdot CO_2\vdots H,R\cdot CO_2\vdots M$; the position of the equilibrium for the free acid will be dependent on the specific nature of the acid and on the character of the solvent, the latter influencing the relative stability of the two modifications by the formation of solvates; thus, with trichloroacetic acid in aqueous solution, the hydrate, $CCl_3\cdot CO_2\vdots H,(OH_2)_n$, is stable, whereas in alcoholic solution, the alcoholate, $CCl_3\cdot CO_2\vdots H,(C_2H_6O)_n$, is unstable and tends to change into the stable alcoholate,

$$CCl_3\cdot CO\cdot OH,(C_2H_6O)_n$$

(compare preceding abstract). The position of equilibrium between the two modifications of a carboxylic acid will be directly connected with the strength of the acid, so that with successive replacement of the hydrogen in acetic acid by chlorine, the absorption spectrum of the product in the pure condition or in solution in light petroleum will gradually approach that of the salts; with a very strong acid such as trichloroacetic acid, the constitution under the conditions named will be exclusively of the true acid type, and the absorption will therefore be identical with that of the salts, as experiment actually shows. On account of impurities difficult to remove, the identity of the absorption curves for all salts of the same acid has occasionally not been realised, but with pure materials, the simplicity of the relations becomes evident (compare Hantzsch, A., 1913, ii, 893; 1914, ii, 5, 230). Confirmatory details are given of the results of spectrum absorption experiments and considerations with acetic acid, chloroacetic acid, and formic acid, their salts and esters, whilst in analogy with the above considerations, nitric acid is represented by the two constitutional formulæ $NO_2\cdot OH$ and $NO_3\vdots H$, from which the esters and salts are respectively derived.

In explanation of the noteworthy fact that alcohol affects the optical properties of the salts of fatty acids in a similar manner to, but in a less degree than those of the free acids, it is suggested that whereas in aqueous solution the salts correspond with the true acid constitution, the effect of alcohol is to cause a partial transformation of the "true salts," $R\cdot CO_2\vdots M$, into "pseudo-salts" of the structure $R\cdot CO\cdot OM$; the tendency to the formation of pseudo-salts will be greater the less positive the nature of the cation and the less negative the nature of the anion.

The suggestion is made that the simultaneous attachment of an ionisable hydrogen (or metal) atom at two oxygen atoms, which is termed the "ionogenic condition," is of greater significance than the mere presence of hydrogen ion or the occurrence of ionisation; for example, ethyl diazoacetate is extremely rapidly decomposed by trichloroacetic acid in light petroleum, whereas in alcohol the reaction is exceedingly slow, and in ethereal solution does not occur at all; the difference in behaviour is due to the difference between the true acid and pseudo-acid modifications of trichloroacetic acid, and the catalytic effect commonly attributed to hydrogen ion is in reality due to the hydrogen atom ionogenically fixed in the molecule of the true acid (see also Snethlage, A., 1915, ii, 615, 825). Mere ionisation causes no alteration in the optical absorptive properties of a substance, but this absence of alteration is characteristic also of the conversion of transparent metallic salts into aquo-salts and of the formation of hydrates and solvates; any apparent exceptions to this rule are to be attributed to chemical or structural change in the acid, as described above for the fatty acids; this also under the influence of solvate formation accounts for the frequently observed effect of solvents which otherwise might be expected to be without action on the ultra-violet absorption of the solute. D. F. T.

**The Hypothesis of the Existence of a Third Simple Radioactive Substance in the Uranium Pleiad.** A. Piccard (*Arch. Sci. phys. nat.*, 1917, [iv], **44**, 161—164).—The hypothesis is that actinium is not derived from either uranium-*I* or uranium-*II*, but from a third isotope of uranium, called Actinuranium (AcU), which does not belong to the uranium–radium family, but is a primary radio-element at the head of the actinium family, with atomic weight greater than that of uranium. If 238 is the atomic weight of uranium-*I* and 240 that of actinouranium, the actual atomic weight found for uranium, 238·16, would be explained, and also how it is that the atomic weight of radium and of lead, derived from uranium-*I*, are respectively exactly 226 and 206. It is considered incomprehensible and without analogy to suppose that an atom can transform itself in two different ways by emitting an $\alpha$-particle, and uranium-*Y* is regarded as the product of the $\alpha$-ray change of actinouranium. In the Geiger-Nuttall relation the values of the constants are the same for all members of the same family, and the difference in the constants for the radium and actinium families indicates that the actinium family is completely distinct from that of the radium family. F. S.

**Electrical Double Refraction in Binary Liquid Mixtures.** C. Bergholm (*Ann. Physik*, 1917, [iv], **53**, 169—176).—The variation of the electric double refraction of binary mixtures with the composition has been examined in the case of mixtures of carbon disulphide and *m*-xylene, carbon disulphide and carbon tetrachloride, chlorobenzene and carbon tetrachloride, chlorobenzene and *m*-xylene, and also carbon disulphide and chloroform. The data obtained for the first pair of liquids agree with the values calculated from the mixture rule, but this does not express the behaviour of the remaining pairs of liquids. H. M. D.

**Influence of Pressure on the Electrical Conductivity of Pure Metals according to E. Grüneisen's Theory. II.** BENGT BECKMAN (*Physikal. Zeitsch.*, 1917, **18**, 507—509. Compare A., 1915, ii, 134).—The influence of pressure on the electrical conductivity of thallium, tantalum, molybdenum, and tungsten has been measured for pressures varying from 700 to 2000 atmospheres. The pressure-coefficient found by experiment is in all cases greater than the value derived from Grüneisen's theory. H. M. D.

**Transmission of a Detonation in Liquid Explosives.** R. BECKER (*Zeitsch. Elektrochem.*, 1917, **23**, 304—308).—A theoretical paper, in which the elevation of temperature produced in ethyl ether (i) by adiabatic compression, and (ii) by a compression wave, is deduced. The value is calculated by formulæ which are derived in the paper for pressures between 100 and 100,000 atmospheres. The following values of $(T_2-T_1)$ are obtained (i) for adiabatic compression: 100 atms., 1·6°; 1000 atms., 15·6°; 10,000 atms., 85°; and 100,000 atms., 245°; (ii) for a compression wave: 100 atms., 1·6°; 1000 atms., 15·6°; 10,000 atms., 113°; and 100,000 atms., 975°. These calculations are made on the basis that $C_p$ is constant and that the Tammann equation of condition is valid. As a result of the calculations, it is suggested that the detonation of glyceryl nitrate is to be explained by the rise of temperature which accompanies the enormous increase of pressure. J. F. S.

**Molecular Attraction. XV. Specific Heats of the Elements and some Energy Changes. II.** J. E. MILLS (*J. Physical Chem.*, 1917, **21**, 623—643. Compare A., 1917, ii, 356).—The atomic heat curves of a number of elements are compared, and it is shown that if the total energy required to raise a monatomic element from absolute zero and transform it into liquid at the melting point is divided by the absolute melting temperature a number is obtained which is nearly the same as the specific heat of the liquid element at its melting point. The energy contents of liquid elements at their respective melting points are approximately proportional to the absolute melting temperatures. The values fall between $7·5T$ and $8·5T$ calories per gram atom.

On the assumption that the attractive forces between molecules operate in accordance with the inverse square law, it is possible to calculate the energy contents of the liquid elements at their melting points, the results so obtained being generally in good agreement with the values derived from the atomic heat curves and the latent heats of fusion. H. M. D.

**Isothermals of Diatomic Substances and their Binary Mixtures. XIX. A Preliminary Determination of the Critical Point of Hydrogen.** H. Kamerlingh Onnes, C. A. Crommelin, and P. G. Cath (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 178—184).—The development of the hydrogen vapour thermostat for the maintenance of low temperatures within ±0·01° has enabled the authors to determine the critical temperature and pressure of hydrogen. The values recorded are $T_c = 33{\cdot}18°$ (abs.) and $p_c = 12{\cdot}80$ atm.

The equation of the rectilinear diameter is $y = +0{\cdot}04416 - 0{\cdot}000398T$, which gives $d_c = 0{\cdot}0310$ for the critical density.

H. M. D.

**The Critical Temperature and Pressure of Mercury and Phosphorus.** J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 138—148).—In the light of the measurements of the vapour pressures of mercury recorded by Cailletet, Colardeau, and Rivière, the author has recalculated the critical data, the values obtained being $T_c = 1172°$ (absolute), $p_c = 180$ atmospheres, and $d_c = 3{\cdot}3$. The values of $b_c = 149 \times 10^{-5}$ and of $\sqrt{a_c} = 10{\cdot}74 \times 10^{-2}$ are also recorded.

The fact that a much higher critical temperature (1260°) was obtained in a previous paper (A., 1916, ii, 610) is attributed to anomalies in the behaviour of mercury at temperatures below 500°.

The available data for the vapour pressure of liquid phosphorus lead to $T_c = 948°$ (absolute) and $p_c = 80$ atmospheres. H. M. D.

**Physical Behaviour and Molecular Properties of Liquids.** W. Herz (*Zeitsch. Elektrochem.*, 1917, **23**, 301).—In previous papers (A., 1915, ii, 682, 823; 1917, ii, 194) the author has shown that the solubility of organic liquids is dependent on the molecular diameter, and that the molecular diameter increases regularly with the number of carbon atoms in the molecule. In the present paper the author continues his theoretical researches. It is shown that the latent heat of vaporisation in homologous series decreases with increasing number of carbon atoms in the molecule and also with increasing molecular diameter. It is also shown that the dielectric constant for homologous series of organic liquids decreases with increasing number of carbon atoms and with increasing molecular diameter.

J. F. S.

**Molecular Association of Compounds of Carbon, Hydrogen, and Oxygen deduced from the Boiling Point and the Density at the Temperature.** W. P. Jorissen (*Chem. Weekblad*, 1917, **14**, 1022—1025).—The number of atoms in the molecule ($n$) of certain hydrocarbons and oxy-derivatives is given by the expression $n = (193M^2)/(T^2_{bp} \cdot d_{bp})$, in which $M$ is the molecular weight, $T_{bp}$ the absolute boiling point at one atmosphere, and $d_{bp}$ the density at the boiling point. A. J. W.

**The Boiling Point Line of the System: Hexane-Nitrobenzene.** E. H. Büchner (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 322—325).—When the boiling point of the mixture is plotted against the molecular proportion of nitrobenzene, a curve is obtained which indicates that the initial rate of increase in the temperature is large by comparison with the slow rate of increase for solutions containing 10—60% of nitrobenzene. The curve is inflected, and rises sharply as the proportion of nitrobenzene is further increased. This form of curve has been found previously for several pairs of liquids of limited miscibility at temperatures above the critical solution temperature.

The boiling point data indicate that this pair of liquids does not exhibit a maximum vapour pressure. This is in agreement with the general rule according to which such maxima are not to be expected when the boiling points of the components differ by more than about 100°. H. M. D.

**The Diffusion of Mercury Vapour in a Vacuum.** Marcel Guichard (*Bull. Soc. chim.*, 1917, [iv], **21**, 237—238).—To prevent the diffusion of mercury vapour from the pump to a tube, which contains a substance capable of absorbing mercury vapour and is being evacuated, it is advised either to introduce a second tube containing the same substance between the experimental tube and the pump, or to interpose a tube cooled sufficiently to cause the mercury vapour to condense. W. G.

**Kinetic Theory of the Ideal Dilute Solution.** S. A. Shorter (*Phil. Mag.*, 1917, [vi], **34**, 521—525).—A criticism of the arguments set forth by Tinker in a recent paper on the theory of binary liquid mixtures (A., 1917, ii, 294). This theory, which is based on the application of the Dieterici equation to binary mixtures, was said to lead to Raoult's law. The author points out that the deduction involves a mathematical error, and when this error is corrected, the theory yields a relation which is quite different from Raoult's law. A similar error is involved in the deduction of the expression for the osmotic pressure of a dilute solution, and the supposed agreement between observation and theory is fictitious. The failure of the theory when applied to actual facts is attributable to the circumstance that it takes no account of changes in the intermolecular forces which ensue when the solute is added to the solvent. H. M. D.

**Kinetic Theory of the Ideal Dilute Solution.** Frank Tinker (*Phil. Mag.*, 1917, [vi], **34**, 526—527).—A reply to Shorter's criticism of the author's theory (compare previous abstract). H. M. D.

**The Structure of the Crystalline Forms of Silica, Iron Disulphide, Zinc Sulphide, and Calcium Carbonate.** J. Beckenkamp (*Centr. Min.*, 1917, 353—365, 393—407. Compare A., 1917, ii, 296).—The axial ratios of quartz and of tridymite are very closely related to those of rhombohedra derived from the cube, one diagonal of the cube being considered the trigonal axis of the rhombohedron. The author considers that the structures of these crystals as well as those of pyrites, zinc blende, sodium and potassium chlorides, calcspar, etc., are closely related to the face-centred cubic lattice. This conclusion is in agreement with the author's theory of the relationship between the atomic weights of the elements and the sizes of the spheres of influence of the atoms which determine the inter-atomic distances in the crystal. The author does not accept the structure for quartz suggested by Bragg.

E. H. R.

**The Colloidal Nature of Colophony. I.** Ludwig Paul (*Kolloid Zeitsch.*, 1917, **21**, 115—121).—See this vol., i, 25.

**Stability of Emulsions in the Constricted Tube and Marble Device for Anaerobiosis.** Ivan C. Hall (*J. Physical Chem.*, 1917, **21**, 609—622).—The stability of oil–water emulsions in certain forms of culture tube has been found to be due to the protection from evaporation which these devices afford. Methods for the distinction of disperse phase from dispersive medium are discussed. [See also *J. Soc. Chem. Ind.*, 1917, **37**, 13a.]

H. M. D.

**The Temperature of Ignition of Gaseous Mixtures.** James Wallace McDavid (T., 1917, **111**, 1003—1015).—In most of the methods previously employed for the determination of the ignition-temperature, the possibility is not excluded that slow combustion occurs before the ignition-temperature is reached, with the result that sufficient heat is generated to raise the remainder of the gaseous mixture to its ignition point. A new method is described in which the time factor is eliminated as far as possible, the method consisting in the ignition of a small volume of the gaseous mixture, contained in a soap bubble, by means of an electrically heated wire or other red hot body, the temperature being noted at which ignition just takes place.

The ignition temperatures of mixtures of various inflammable gases with air have been determined, and the results obtained show that the method not only gives a sharp ignition point, but that it is very suitable for comparative determinations. When the soap bubbles are not too large, instantaneous ignition occurs, and the ignition temperatures obtained under these conditions are regarded as the true values. When larger bubbles are used, the inflammable mixture ignites at a somewhat lower temperature, but this is probably due to the fact that slow combustion precedes the ignition, which is quite perceptibly delayed.

H. M. D.

**The "Uniform Movement" during the Propagation of Flame.** Walter Mason and Richard Vernon Wheeler (T., 1917, **111**, 1044—1057).—According to the theoretical considerations advanced by Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 274), the speed of the "uniform movement," which characterises the propagation of flame through inflammable mixtures under suitable conditions, should be directly proportional to $(T-t)$ and inversely proportional to $(t-\theta)$, where $T$ is the combustion temperature, $t$ the ignition temperature, and $\theta$ the initial temperature of the combustible mixture, provided that the mixtures considered have the same thermal conductivity.

In order to obtain data to test this conclusion, measurements have been made of the velocity of the "uniform movement" in a series of mixtures of methane, oxygen, and nitrogen. The ignition temperatures have also been determined and the combustion temperatures calculated. It is found that the above relation is very nearly true so long as the oxygen in the mixtures is in excess of that required for complete combustion. When the amount of oxygen present is less than this, the observed velocity of the "uniform movement" is less than that calculated from the ratio $(T-t)/(t-\theta)$. In the case of upper limit mixtures, the deviation is considerable. From this it is inferred that the calculated combustion temperature is not attained when the oxygen is deficient in quantity, for in these circumstances the combustion process is more protracted, and there is consequently an increased radiation loss through the walls of the tube during the propagation of the flame.

With regard to the influence of the diameter of the tube on the speed of the "uniform movement," Mallard and Le Chatelier arrived at the conclusion that the speed will not be appreciably affected if the diameter is sufficiently great. This is probably true for tubes from 5 to 10 cm. in diameter, but in wider tubes the influence of convection currents introduces a factor which affects the speed to a considerable extent. Measurements of the speed for mixtures of methane and air in tubes varying from 2·5 to 96·5 cm. in diameter show that convection effects increase the speed in the wider tubes. It would thus seem that the "uniform movement" is a strictly limited phenomenon obtainable only in tubes of which the diameter is large enough to prevent appreciable cooling by the walls, but small enough to suppress the disturbing influence of convection.

The conditions necessary for obtaining the "uniform movement" of flame are discussed, and, in particular, attention is directed to the importance of the method of ignition. H. M. D.

**Kinetics of the Alkaline Saponification of the Esters of Carbonic Acid.** ANTON SKRABAL (*Monatsh.*, 1917, **38**, 305—318). —The rate of saponification of methyl and ethyl carbonate has been investigated at 25° in solutions containing sodium carbonate. The progress of the reaction, which may be represented by the equation $R_2CO_3 + Na_2CO_3 + 2H_2O = 2NaHCO_3 + 2ROH$, was followed by titration with $0·1N$-hydrochloric acid in presence of phenolphthalein. The results obtained show that the rate of saponification of the esters is proportional to the concentration of the ester and of the hydroxyl ion. For the methyl ester, the bimolecular velocity coefficient $k = 5·4$, and for the ethyl ester

$k = 1 \cdot 6$. These numbers are of the same order of magnitude as the coefficients for the corresponding esters of acetic acid. In acid solution, the esters are hydrolysed very slowly.

Experiments made with sodium ethyl carbonate show that the second stage of the alkaline saponification takes place with very great velocity, and that this is also characteristic of the hydrolysis in acid solution. The kinetic data are discussed in reference to the constitution of carbonic acid, and in explanation of the relative rates of the first and second stages of hydrolysis, it is suggested that the second stage is not really a hydrolytic process, but is to be regarded as an intramolecular change corresponding with the equation $OH \cdot CO \cdot OR = CO_2 + R \cdot OH$. H. M. D.

**The Velocity of the Alkaline Saponification of Formic Esters.** ANTON SKRABAL and ADOLF SPERK (*Monatsh.*, 1917, **38**, 191—201).—The rate of saponification of methyl and ethyl formate has been measured at 0° and at 25° by using a mixture of potassium iodide and iodate as dynamic regulator. In view of the fact that the esters form additive compounds with potassium tri-iodide, the active mass of the ester during the later stages of the reaction is less than that which would be calculated from the thiosulphate titrations of the liberated iodine. For this reason, the calculated saponification velocity coefficient falls as the reaction proceeds, and the correct values can only be obtained from the initial stages. These initial measurements give $k = 2 \cdot 4 \times 10^3$ for methyl formate and $k = 1 \cdot 4 \times 10^3$ for ethyl formate at 25°. These values are in agreement with those previously obtained by indirect measurements according to an electrochemical method (Eucken, A., 1910, ii, 279). H. M. D.

**Consecutive Reactions. The Saponification of Methyl Oxalate in Solutions containing Iodide and Iodate.** ANTON SKRABAL (*Monatsh.*, 1917, **38**, 159—189).—In the use of regulator mixtures for controlling the concentration of one of the reacting substances or one of the reaction products during the progress of a reaction, it is necessary to distinguish between static and dynamic regulators. In the case of static regulators, the velocity of the regulator reaction is very large in comparison with that of the reaction investigated, whilst the velocity of the regulator reaction may be of the same order or even much smaller than that of the reaction under examination if the regulator mixture is of the dynamic type. It is shown that the progress of a reaction which is regulated by a mixture of the dynamic group is such that the velocities of the two are mutually influenced in such a way that they keep in step. Whilst a mixture of the salts $Na_2HPO_4$ and $NaH_2PO_4$ acts as a static regulator in controlling the hydrogen ion concentration of a solution, a mixture of potassium iodide and iodate behaves as a dynamic regulator.

This mixture has been used in the determination of the velocity coefficients corresponding with the first and second stages in the saponification of methyl oxalate. From the observed rate at which iodine is formed, it is possible to calculate the saponification coefficients. The experiments with methyl oxalate and potassium methyl oxalate give $k=1{\cdot}2\times10^6$ for the first stage and $k=1{\cdot}94\times10^2$ for the second stage respectively. These values agree satisfactorily with those obtained in previous measurements, in which use was made of a static regulator.

Comparison of the two series of experiments shows that the determination of the rate of saponification of methyl oxalate can be effected much more conveniently and accurately by using an iodide-iodate mixture as regulator than by the use of a mixture of sodium dihydrogen and disodium hydrogen phosphate. It is probable that the use of iodide-iodate mixtures may be found useful in the investigation of many other reactions which proceed with conveniently measurable velocity when the hydrogen ion concentration is not far removed from that corresponding with the neutral point. H. M. D.

**History of Catalysis.** H. J. Prins (*Chem. Weekblad*, 1917, **14**, 1000—1004).—A polemical paper in support of the author's views on catalysis, and criticising Böeseken's "dislocation theory." A. J. W.

**Contact Catalysis. II. Fractional Combustion.** Wilder D. Bancroft (*J. Physical Chem.*, 1917, **21**, 644—675. Compare A., 1917, ii, 566).—The paper consists for the most part of extracts from the literature relating to the fractional combustion of gases, and attention is directed to the circumstance that these observations afford many examples of the selective influence of catalysts in determining the nature of the final products. At low temperatures, the influence of solid catalysts is very marked, and is one of the chief factors in determining which of two combustible gases will burn the more rapidly. At high temperatures, the influence of solid catalysts is greatly reduced and may be negligible, the reaction in this case taking place in the gaseous phase.

By suitably varying the solid catalyst, it should be possible to realise all the possible intermediate stages in the fractional combustion of a mixture of two combustible gases from the complete combustion of the one to the complete combustion of the other. H. M. D.

**Contact Catalysis. Decomposition of Ethyl Alcohol.** Carl J. Engelder (*J. Physical Chem.*, 1917, **21**, 676—704).—When the vapour of ethyl alcohol is passed over heated metallic oxides or finely divided metals, it decomposes with the formation of ethylene and water or acetaldehyde and hydrogen, and the relative quantities of the two sets of products vary with the nature of the solid catalyst.

Experiments made with alumina, silica, zirconium dioxide, and titanium dioxide show that the ratio of ethylene to hydrogen in the product of the reaction is reduced by mixing the alcohol with water. Similarly, it has been found that the addition of hydrogen to the alcohol vapour increases the proportion of ethylene when titanium dioxide is used as catalyst. Further observations with this catalyst at 400° show that acetaldehyde is not decomposed to any great extent into methane and carbon monoxide, but that it promotes the formation of ethane by combination of ethylene and hydrogen.

Ethyl ether when passed over alumina at 380° is decomposed almost quantitatively into ethylene and water. With titanium dioxide, the dehydrating action takes place very slowly. At 210°, ethyl alcohol, when passed over alumina, gives ethyl ether as the chief product. H. M. D.

**The Determination of Atomic Weights.** MARCEL GUICHARD (*Bull. Soc. chim.*, 1917, [iv], **21**, 238—241).—A general criticism of the methods used for determining atomic weights. Three conditions for such methods are given, namely: (1) as far as possible, analyse or synthesise oxygenated compounds; (2) perform simple chemical reactions only requiring a very small number of auxiliary substances, avoiding contact with water, air, or inert gases; (3) use complete methods, where all the compounds utilised or formed are weighed. W. G.

**Variable Atomic Weights, with some Reference to Geologic Time.** H. S. SHELTON (*Chem. News*, 1917, **116**, 259—261).—A criticism of the theory of isotopes in which the author contends that the known facts do not warrant the conclusion that isotopic elements are inseparable.

Estimates of geologic time based on radioactivity data are probably not nearly so precise as the statements of certain workers on radioactive problems would suggest. In view of the possible errors which are inherent in such estimates, it is considered that the radioactivity estimates are only of value in indicating the order of geologic eras. H. M. D.

**Atomic Frequency and Atomic Number. Frequency Formulæ with Empirical Constants.** H. STANLEY ALLEN (*Phil. Mag.*, 1917, [vi], **34**, 478—487).—It is probable that some connexion exists between the characteristic frequency $\nu$ of an element in the solid state and its atomic number $N$, and an attempt is made to establish this by making use of the various formulæ which have been put forward to express the relation between the atomic frequency and other physical properties. These formulæ are more or less empirical, and in some cases yield values for the atomic frequency which differ appreciably. For the majority of the elements, however, the calculated frequencies are found to satisfy the relation $N\nu = n\nu_A$, in which $n$ is a whole number (the frequency number) and $\nu_A$ a constant. The same element may have different frequency numbers for the different forms of the solid element, but, broadly speaking, the value of $n$ varies in a periodic manner with the atomic number. The mean value of $\nu_A$ for the metallic elements is $21{\cdot}3 \times 10^{12}$. H. M. D.

**Electronic Frequency and Atomic Number.** H. STANLEY ALLEN (*Phil. Mag.*, 1917, [vi], **34**, 488—496. Compare preceding abstract).—The electron frequencies calculated from the maximum of the selective photo-electric effect, from the limiting photo-electric frequency, from the ionisation potential of gases, and from thermionic potentials appear to be related in a simple manner with the atomic number $N$ of the element concerned. If $\nu$ is the calculated electron frequency, then $N\nu = n\nu_E$ or $N\nu = (n + \frac{1}{2})\nu_E$, in which $n$ is an integer and $\nu_E$ is the fundamental electronic frequency $= 3{\cdot}289 \times 10^{15}$. The fundamental electronic frequency is thus about 154 times the fundamental atomic frequency $\nu_A$. H. M. D.

**Formulation of the Law of Multiple Proportions.** D. BALAREFF (*J. pr. Chem.*, 1911, [ii], **95**, 397—398).—It is pointed out that it is only in the case of simple series of compounds of two elements that the masses of the one element which unite with the same mass of the other element are to one another in the ratio of simple integers. For example, whilst the masses of carbon which unite with one part of hydrogen are in methane, ethylene, and acetylene respectively 3, 6, and 12, in methane, ethane, propane, hexane, eicosane, and anthracene they are 3, 4, 4·5, 5·143, 5·714, and 16·8. It would be better, therefore, to express the law as "The masses of the different elements in a compound are directly proportional to their equivalent weights or to simple multiples of their equivalents." J. C. W.

**Absolute Determinations of Mass by means of the Micro-balance.** J. KRAMER (*Chem. Zeit.*, 1917, **41**, 773—774).—The ordinary form of torsion micro-balance is not suitable for direct weighings, and experiments have accordingly been made to ascertain the applicability of a balance of the usual type in the determination of the weights of small quantities of substance. The balance described has a carrying capacity of 1 gram, the length of the beam is 154·4 mm., and its weight 7·825 grams. The addition of 0·1 mg. produces a displacement of the pointer amounting to 48 divisions when the balance is unloaded, and this decreases to 35 divisions for a load of 100 mg. and to 10 divisions for a load of 1000 mg. Each division on the scale represents 0·35 mm.

The results obtained with the balance, when suitable precautions are taken, are said to be quite satisfactory. H. M. D.

**Exact Weighings.** MARCEL GUICHARD (*Bull. Soc. chim.*, 1917, [iv], **21**, 233—235).—An examination of the temperature differences between the two arms of a balance, due to the variation of external conditions. W. G.

**The Limitations of the Balance.** BERTRAM BLOUNT (T., 1917, **111**, 1035—1039).—Series of weighings made by three independent observers on six balances of the best make showed variations ranging from 0·4 to 1·6 mg. during a period of four months. These variations cannot be correlated with any known variation in the external conditions. The author is inclined to attribute the observed inconstancy to variations in the effective length of the arms of the balance resulting from fortuitous movements of the knife-edges. H. M. D.

**The Weighing of Evacuated Tubes.** MARCEL GUICHARD (*Bull. Soc. chim.*, 1917, [iv], **21**, 235—237).—The author prefers to use a sealed tube rather than one closed by a tap, and describes a method of weighing such an evacuated tube, filling it with gas, and determining the weight of gas thus entering. W. G.

**The Centenary of Charles Gerhardt.** (*Suppl. Bull. Soc. chim.*, 1916, 1—108).—An account of the proceedings of the meeting of the Société chimique de France on December 8th, 1916, in celebration of the centenary of Charles Gerhardt. There is included in it a full account of Gerhardt's life and work by M. Marc Tiffenau, and a chronological list of his publications.

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## Inorganic Chemistry.

**Action of Hydrogen Peroxide Solution on Lime-water and Iodine: Preparation of Ammonium Iodide.** T. C. N. BROEKSMIT (*Pharm. Weekblad*, 1917, **54**, 1373—1374).—In presence of hydrogen peroxide solution, iodine reacts with lime-water to form the iodide, with evolution of gas, and formation of only a trace of iodate. With ammonium hydroxide the reaction takes place in accordance with the equation $2NH_3 + I_2 + H_2O_2 = 2NH_4I + O_2$. A. J. W.

**Reaction between Ozone and Hydrogen Peroxide.** VICTOR ROTHMUND and ALEXANDER BURGSTALLER (*Monatsh.*, 1917, **38**, 295—303. Compare A., 1913, ii, 773).—The velocity of the reaction between ozone and hydrogen peroxide has been examined in 0·01*N*-sulphuric acid solution at 0°, the two substances being separately estimated in the reaction mixture by the method described in a previous paper (A., 1913, ii, 524). In presence of relatively large quantities of hydrogen peroxide, the reaction may be represented by the equation $H_2O_2 + O_3 = H_2O + 2O_2$, and the rate of disappearance of the ozone follows closely the equation for a unimolecular reaction. When the ratio of hydrogen peroxide to ozone is smaller, the ozone disappears more rapidly than the hydrogen peroxide, and this inequality in the quantities of ozone and hydrogen peroxide which are destroyed in a given interval of time increases as the concentration of the hydrogen peroxide is reduced.

The facts suggest that the interaction between ozone and hydrogen peroxide is accompanied by the spontaneous decomposition of ozone and that hydrogen peroxide acts as a powerful catalyst in respect to the latter reaction. This theory also offers an explanation of previously recorded observations on the rate of decomposition of ozone in dilute sulphuric acid solution (compare A., 1913, ii, 489), for it is highly probable that the ozonisation of oxygen is accompanied by the formation of traces of hydrogen peroxide.

H. M. D.

**The Valencies of Nitrogen.** Franz Wenzel (*Monatsh.*, 1917, **38**, 267—293).—The author considers that no conclusive evidence has yet been put forward in support of the view that four of the nitrogen valencies bear the same relation to the fifth. Whilst certain chemical observations suggest that there are two pairs of valencies which are identical in relation to the fifth valency, physico-chemical data seem to indicate that there are three valencies which are identical with regard to the fifth valency. From this it is inferred that the fifth valency does not always represent one and the same valency unit.

An attempt is made to account for the behaviour of nitrogen compounds on the assumption that the valencies of nitrogen are divisible into two distinct groups, one of which includes two and the other three valencies which are equal in all respects. When quinquevalent nitrogen is transformed into tervalent nitrogen there is a loss of one valency from each group. This change is supposed to result in the formation of an intra-atomic double linking connecting dissimilar nuclei. In support of this theory attention is directed to the similarity between the amines and ethylene derivatives in respect of their capacity to form additive compounds.

It is said that this hypothesis affords a satisfactory account of the chemistry of nitrogen compounds. H. M. D.

**Disodium Nitrite, an Additive Compound of Sodium Nitrite and Sodium.** Edward Bradford Maxted (T., 1917, **111**, 1016—1019).—When solutions of metallic sodium and sodium nitrite in anhydrous ammonia are mixed together, a brilliant, yellow substance is precipitated which has the composition $Na_2NO_2$. The same substance is deposited on the cathode when a solution of sodium nitrite in perfectly anhydrous liquid ammonia is subjected to electrolysis. The substance is decomposed vigorously by water with the formation of sodium nitrite, sodium hydroxide, and hydrogen. By passing a current of moist nitrogen over the disodium nitrite, the action is moderated, and the resulting solution is found to be free from hydroxylamine and hyponitrite.

H. M. D.

**Formation of Large Crystals in Zinc Rods and Wire.** W. Fraenkel (*Zeitsch. Elektrochem.*, 1917, **23**, 302—304).—It has been observed that large crystals are often found in zinc rods which have been worked mechanically. The author describes experiments made with the object of ascertaining the conditions under which these large crystals are formed and the reasons for their formation. Rods of zinc of varying diameter were subjected to a temperature just below the melting point of zinc for some time, and after cooling were broken and the structure of the break examined. In some cases it was found that a recrystallisation of the metal had occurred, and that the cross-section of the break consisted of a single crystal, whilst in other cases only small crystals were observed. The author suggests possible explanations of the phenomenon, but is unable to decide on any one of the suggestions as the cause. A number of microphotographs of sections of zinc rods before and after treatment are given in the paper. J. F. S.

**Action of Hydrogen Peroxide on the Neutral Salts of Lead.** V. Zotier (*Bull. Soc. chim.*, 1917, [iv], **21**, 241—243. Compare A., 1913, ii, 216, 465).—Neutral lead salts exert a more or less marked catalytic action on hydrogen peroxide. Using hydrogen peroxide (100 vols.), the catalysis is intense with soluble organic salts, and feeble with insoluble organic salts or mineral salts. With lead acetate one portion of the hydrogen peroxide yields lead peroxide, which then reacts with the remainder of the hydrogen peroxide, and at the end of the reaction there is no lead peroxide left. If the solid salt is used, the catalysis is at first moderate, but soon becomes violent and the mass becomes hot. The presence of acids lessens or hinders the catalysis by hindering the preliminary formation of the lead peroxide. [See also *J. Soc. Chem. Ind.*, 1918, **37**, 7A.]
W. G.

**Some Compounds of Lead.** V. Zotier (*Bull. Soc. chim.*, 1917, [iv], **21**, 244—246. Compare A., 1913, ii, 216, 465, and preceding abstract).—Pure lead peroxide may be prepared by the addition of hydrogen peroxide to a solution of lead nitrate in 20% sodium hydroxide. Hydrogen peroxide may be used to differentiate between a normal and a basic lead salt. With the former it does not give any residual lead peroxide, but with the latter it does. Alkaline solutions of lead salts may be used as a delicate test for hydrogen peroxide, or conversely hydrogen peroxide in the presence of sodium hydroxide may be used as a delicate test for lead.

Contrary to the general opinion, it is found that lead peroxide is slowly attacked by mineral acids or aqueous solutions of alkali hydroxides. The process is, in all cases, very slow, the rate varying with the acid or alkali used.

By heating together at 150° equal weights of lead nitrate and 50% sodium hydroxide, an amorphous red lead is obtained, but if the proportion of lead salt is halved and the temperature raised to 160°, a microcrystalline red oxide is obtained. [See also *J. Soc. Chem. Ind.*, 1918, **37**, 7A.] W. G.

**The Dissociation Constants of Mercury Hydroxides.** I. M. Kolthoff (*Chem. Weekblad*, 1917, **14**, 1016—1022).—The dissociation of mercury hydroxide solution is a step-by-step process, and can be represented by the scheme

$$Hg(OH)_2 \rightleftharpoons HgOH^{\cdot} + OH'; \; HgOH^{\cdot} \rightleftharpoons Hg^{\cdot\cdot} + OH'.$$

A. J. W.

**Quantitative Investigations on the Corrosion of Resistant Glass by Sodium Hydroxide.** C. J. van Nieuwenburg (*Chem. Weekblad*, 1917, **14**, 1034—1040).—A comparison of the effects produced by heating sodium hydroxide solution in Jena and Laborax flasks. A. J. W.

**The Production of Colloidal Base Metals by Reduction of Solutions or Suspensions of Compounds at Higher Temperatures in the Presence of Protective Substances. Colloidal Nickel.** C. Kelber (*Ber.*, 1917, **50**, 1509—1512).—The knowledge that near 200° nickel oxide and some nickel salts can be reduced to metallic nickel by hydrogen, has been applied to the production of colloidal nickel by reducing solutions or suspensions in glycerol containing gelatin or gum arabic as a protective colloid. For example, a solution of nickel formate and gelatin in glycerol at 200—210° when submitted to the action of a stream of hydrogen assumes a chestnut-brown colour. The colloidal solution remains unaltered in the air and is miscible with alcohol, but on treatment with water and centrifuging deposits the colloidal metal as a dark brown solid, containing 25—30% of nickel, which can again yield colloidal nickel solutions in dilute acetic acid, acidified water, glycerol, or alcohol.

Other reducing agents can be applied to the same purpose; nickel formate at 220° in glycerol solution in the presence of gelatin, is reduced by hydrazine hydrate with formation of a colloidal nickel solution of similar properties to that just described. Formaldehyde, hydroxylamine, and hypophosphorous acid can also be applied as reducing agents for the purpose, whilst gum arabic can be used in place of gelatin. The nickel formate can be replaced by nickel acetate or freshly precipitated nickel hydroxide. D. F. T.

**Iso- and Hetero-poly-acids. XV. Critical Researches on the Constitution of the Hetero-poly-acids.** Arthur Rosenheim and Johannes Jänicke (*Zeitsch. anorg. Chem.*, 1917, **100**, 304—354. Compare A., 1913, i, 413; ii, 59; 1914, ii, 58; 1915, ii, 266, 468; 1916, ii, 333, 334; 1917, ii, 35).—A historical and theoretical paper in which the crystallographic, physical, and chemical properties of the iso- and hetero-poly-acids are summarised and the whole of the previous work is discussed. The earlier theories on the constitution of these acids are reviewed, including the application of Werner's co-ordination theory. The last is found to be unsatisfactory, but the modification of this theory suggested by Miolati (A., 1908, ii, 595) and extended by Rosenheim provides the most satisfactory elucidation of the constitution of these substances. E. H. R.

## Analytical Chemistry.

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**New Form of Safety Pipette.** A. S. Behrman (*J. Ind. Eng. Chem.*, 1917, **9**, 1047).—A three-way tap is attached to the top of an ordinary pipette by means of a short length of rubber tubing and a rubber bulb fitted with suitable valves is connected with the upper limb of the tap. The pipette is filled by pressing and releasing the bulb. The tap is then turned so as to admit air to the pipette, by which means the level of the liquid is lowered to the mark, and then delivered. W. P. S.

**Preparation of Ammonium Citrate Solution and the Estimation of Insoluble Phosphoric Acid.** Philip McG. Shuey (*J. Ind. Eng. Chem.*, 1917, **9**, 1045).—Neutral ammonium citrate solution may be prepared by dissolving 1814·37 grams of citric acid in 6961 c.c. of water and 1760 c.c. of 28% ammonia, the water and ammonia being measured at 23°. The insoluble phosphoric acid in acid phosphate may be estimated with practically identical results, whether or not the weighed portion has been washed previously with water, and preliminary washing of samples containing cyanamide does not appear to be necessary. It may be important to use a neutral ammonium citrate solution in the case of ground tankage, whale guano, meat guano, fish, and similar materials which have not been strongly acidified. W. P. S.

**Micro-method for the Estimation of Inorganic Phosphates in the Blood-serum.** W. McKim Marriott and F. H. Haessler (*J. Biol. Chem.*, 1917, **32**, 241—243).—Full details of the method previously described (compare Howland, Haessler, and Marriott, A., 1916, ii, 269). H. W. B.

**The Perchlorate Method for the Estimation of the Alkali Metals.** F. A. Gooch and G. R. Blake (*Amer. J. Sci.*, 1917, [iv], **44**, 381—386. Compare A., 1917, ii, 270).—In this method it is unnecessary to use an alcoholic liquid saturated with the substance to be precipitated, since the volume of the solution (97% alcohol containing 0·1% of perchloric acid) used for washing the precipitate may be so restricted that the solubility of the precipitated perchlorates is insignificant. A single evaporation with a moderate excess of perchloric acid (0·1 c.c. for each 0·1 gram of salt) is not sufficient to convert considerable quantities of alkali chlorides (for example, 0·3 gram) completely into perchlorate; the residue should be treated with a further quantity of perchloric acid and again evaporated. For the separation of large amounts of insoluble perchlorates from sodium perchlorate, the washed precipitate should be dissolved in a small volume of water and the evaporation with perchloric acid repeated. In the case of rubidium perchlorate, the precipitate should be digested for fifteen minutes with the alcoholic washing solution. It is to be noted that perchloric acid has a distinct solvent action on glass. [See also *J. Soc. Chem. Ind.*, 1918, **37**, 21A.] W. P. S.

**Micro-method for the Estimation of Calcium and Magnesium in Blood-serum.** W. McKim Marriott and John Howland (*J. Biol. Chem.*, 1917, **32**, 233—239).—Full details of the method previously described (compare Howland, Haessler, and Marriott, A., 1916, ii, 269). H. W. B.

**Estimation of the Metal Content of Powdered Metals.** F. Hodes (*Zeitsch. angew. Chem.*, 1917, **30**, 240).—The quantity of metallic tungsten in powdered tungsten which has been prepared by reduction with carbon may be estimated by igniting a portion of the sample in an open crucible; the increase in weight is due to oxidation of the metal to tungsten trioxide. As, however, the powdered metal usually contains small quantities of carbon and moisture, it is necessary to heat another portion of the sample in a current of oxygen, weigh the amounts of carbon dioxide and water given off, and correct the first weight accordingly. W. P. S.

**Iodometric Estimation of Copper and Iron.** Herm. Ley (*Chem. Zeit.*, 1917, **41**, 763).—Soluble cupric and ferric salts both liberate iodine from potassium iodide in acetic acid solution, and the iodine set free is a measure of the amount of cupric and ferric salts present. When it is desired to estimate copper in the presence of iron, the latter may be precipitated as ferric phosphate, which is insoluble in acetic acid and does not react with potassium iodide; cupric phosphate, however, is readily soluble in acetic acid. The solution containing the cupric and ferric salts is treated with sodium phosphate solution, then acidified with acetic acid, potassium iodide is added, and the iodine is titrated with thiosulphate solution. The ferric salt is estimated by treating another portion of the original solution with potassium iodide and acetic acid, and titrating the liberated iodine; the difference between the volumes of thiosulphate solution used in the two titrations is equivalent to the quantity of ferric salt present. Aluminium and zinc do not interfere.
W. P. S.

**Sensitive Reaction of Hydrogen Peroxide depending on the Formation of Dihydroxytartaric Acid.** G. Denigès (*Ann. Chim. anal.*, 1917, **22**, 193).—A violet coloration is formed when a small quantity of dilute hydrogen peroxide solution is added to a mixture of 2 c.c. of 5% tartaric acid solution and 2 drops of 5% ammonium ferrous sulphate solution, and the mixture then treated with 6 drops of sodium hydroxide solution. The reaction may be obtained with a quantity of hydrogen peroxide not exceeding 0·05 mg. W. P. S.

**Estimation of Glycerol by the Iodide Method, using Small Quantities of Hydriodic Acid (Semimicro-iodide Method).** R. Neumann (*Zeitsch. angew. Chem.*, 1917, **30**, 234—237).—The author finds that this method (compare A., 1902, ii, 111, 585; 1903, ii, 515) yields trustworthy results when only

about one-tenth of the usual quantities of sample and reagents are employed. The apparatus used has about one-eighth of the capacity of the iodide apparatus described by Stritar (A., 1904, ii, 95).
W. P. S.

**Oxidation of Organic Compounds with Chromic Acid.** A. WINDAUS (*Zeitsch. physiol. Chem.*, 1917, **100**, 167—169).—Certain organic compounds readily yield acetone and acetaldehyde when treated with chromic acid. The products can be separated by distillation and recognised by conversion into the comparatively insoluble *p*-nitrophenylhydrazones. In this way, cholesterol, coprosterol, and sitosterol, containing an *iso*propyl group, can be readily distinguished from the somewhat similar bile acids, which do not yield any acetone or aldehyde when oxidised by chromic acid.

Methylpentoses, such as rhamnose, are similarly easily detected in the presence of other pentoses and hexoses by means of the chromic acid oxidation test. The test must be carried out under the prescribed conditions, involving the use of a solution of chromic acid in glacial acetic acid. If an excess of sulphuric acid is substituted for the glacial acetic acid, lævulose, and even dextrose, are found to yield acetaldehyde and other volatile products, which can form iodoform and insoluble *p*-nitrophenylhydrazones (compare Engfeldt, A., 1917, ii, 550).
H. W. B.

**Formaldehyde as a Negative Catalyst in Sugar Reactions.** H. MAGGI and G. WOKER (*Ber.*, 1917, **50**, 1331—1335).—Formaldehyde hinders the reducing action of dextrose or maltose in the Moore-Heller and Rubner tests, and especially the reduction of methylene-blue or picramic acid. Although formaldehyde has a more powerful reducing action on Nylander's solution than the sugars, mixtures of them containing 1 c.c. of 40% formaldehyde to 0·5 c.c. of 1% dextrose or maltose do not affect this reagent. The aldehyde also hinders the reduction of Fehling and Pavy solutions by dextrose or maltose.
J. C. W.

**Malic Acid and Citric Acid.** T. C. N. BROEKSMIT (*Pharm. Weekblad*, 1917, **54**, 1371—1373).—Both malic acid and citric acid answer to the iodoform test, but can be distinguished by the fact that barium malate is not precipitated either in neutral solution or in presence of acetic acid.
A. J. W.

**Probable Accuracy, in Whole Blood and Plasma, of Colorimetric Estimations of Creatinine and Creatine.** ANDREW HUNTER and WALTER R. CAMPBELL (*J. Biol. Chem.*, 1917, **32**, 195—231. Compare Wilson and Plass, A., 1917, i, 360, and Gettler and Oppenheimer, A., 1917, ii, 184).—The authors have prepared a series of curves showing the rate at which the colour utilised as the basis of a creatinine estimation develops, not only in pure aqueous solutions, but also in the various circumstances in which it is applied to the analysis of blood. A comparison of these curves reveals the presence or absence of substances capable of producing a colour similar to that arising from creatinine. In plasma, the only substance capable of simulating the reaction for creatinine is dextrose, and its influence on the estimation of creatinine is shown to be too small to have much practical importance. In whole blood, however, an unknown substance is present which, although reacting more slowly than creatinine, contributes in the Folin technique an appreciable fraction of the total colour developing within ten minutes. On laking the blood, a much larger amount of this unknown substance is set free and passes into the protein-free filtrate. The filtrates from autoclaved blood or plasma also contain relatively large quantities of the substance which reacts similarly to creatinine.

A consideration of these results indicates that although the Folin method estimates the preformed creatinine of plasma with a satisfactory approximation to accuracy, the results obtained by the same method for the preformed creatinine of whole blood are on the average about 50% higher than the truth. The technique of Myers leads to a still greater exaggeration of the preformed creatinine of blood. The Folin method for creatine, whether applied to whole blood or to plasma, also gives decidedly erroneous results, liable to be in the former case about twice and in the latter about four times as high as the amount actually present.

H. W. B.

**Estimation of Fæcal Indole.** Olaf Bergeim (*J. Biol. Chem.*, 1917, **32**, 17—22).—The fæces are mixed with potassium hydroxide solution and the indole distilled over in an ordinary Kjeldahl distillation apparatus. Any ammonia in the distillate is removed by a second distillation after acidifying with dilute sulphuric acid. The final distillate is treated with sodium $\beta$-naphthaquinonesulphonate and alkali, and the blue indole compound formed extracted with chloroform and estimated colorimetrically (compare Herter and Foster, A., 1906, ii, 134, 910). H. W. B.

**Improvement of the Volumetric Method of Estimating Albumin by means of Potassium Ferrocyanide. Presence of Rapidly Decomposable Proteins in certain Urines.** Ed. Justin Mueller (*Bull. Sci. Pharmacol.*, 1917, **24**, 221—224; from *Chem. Zentr.*, 1917, ii, 325. Compare A., 1917, ii, 555).—In the previous communication the author has described a method of estimating albumin in urine, and pointed out that the immediate occurrence of the colour change with iron alum (after addition of 3·5 c.c. of potassium ferrocyanide necessary for the saturation of the acidified water) is indicative of the absence of albumin. Subsequently, however, it has been observed that the colour change can also occur in the presence of readily decomposable proteins. These differ from the albumins known in urology. They do not yield a precipitate when warmed or when treated with acetic acid.

They are precipitated by warm trichloroacetic acid and give precipitates with cold trichloroacetic acid, cold nitric acid, and Esbach's reagent, which gradually dissolve when warmed. A cold solution of potassium ferrocyanide in acetic acid yields a precipitate which is stable when warmed; saturated ammonium sulphate or sodium acetate solution gives a precipitate soluble in water, whilst precipitates are not produced by sodium chloride or magnesium sulphate. The proteins are readily hydrolysed when warmed or in acetic acid solution. They are rendered more stable by addition of ammonium sulphate.

For the volumetric estimation, urine (50 c.c.) is treated with so much finely divided ammonium sulphate (8—9 grams) that a volume of 55 c.c. is attained; the solution is filtered, and 11 c.c. of the filtrate are used for the titration. H. W.

**Adaptation of Winkler's Method to Biological Work.** W. J. V. Osterhout and A. R. C. Haas (*J. Biol. Chem.*, 1917, **32**, 141—146).—The apparatus consists of two glass tubes 30 cm. long and 27 mm. in diameter joined together by rubber tubing and furnished with rubber stoppers at the free ends (all the rubber tubing and stoppers used in the apparatus should be coated with paraffin). One of the rubber stoppers is connected with a series of smaller glass tubes (13 mm. inside diameter) joined by rubber tubing with only enough space between them to permit the insertion of a clamp. The larger tubes are filled with the solution containing the organisms of which the oxygen metabolism is to be investigated. To estimate the oxygen in the solution at any time, the organisms are first allowed to gravitate to the bottom of the two tubes, and then the lower one, containing the organisms, is clamped off and removed. The smaller tubes are then filled successively with alkaline potassium iodide, manganese chloride, and concentrated hydrochloric acid, each being separated from the other by means of the clamps. By releasing the clamps, the reagents are successively introduced into the oxygenated solution, and finally the contents are run into a beaker and titrated with thiosulphate, as in Winkler's method for the estimation of oxygen in solutions.

The advantages claimed for the apparatus are that it permits the removal of the organisms before adding the reagents, and also the addition of the reagents without danger of contamination by oxygen. Modifications are described whereby it is possible to take samples of the solution for analysis at intervals during an experiment. H. W. B.

## General and Physical Chemistry.

**The Arc Spectrum of Tantalum on the International Scale.** Hedwig Josewski (*Zeitsch. wiss. Photochem.*, 1917, **17**, 79—96).—Accurate measurements have been made of the wave-lengths of lines in the arc spectrum of tantalum between $\lambda$ 7000 and $\lambda$ 2430. The observations, which are compared with those obtained previously by Exner and Haschek, also afford information relative to the intensity and the sharpness of the lines.

There is no evidence of the occurrence of pairs of lines with a constant difference of frequency as suggested by Paulson (compare A., 1915, ii, 196). H. M. D.

**The Photographic Spectra of Meteorites.** Sir William Crookes (*Phil. Trans.*, 1917, [*A*], **217**, 411—430).—The spectra of thirty meteorites have been examined with the aid of a spectrograph characterised by certain novel features, which are described. The use of a quartz slit has given very satisfactory results, the difficulty attending the production of a true knife-edge being solved by making a very narrow bevel on the front of the quartz plate and thereby producing a jaw with an angle of 90°. The bevelled edge is quite opaque in consequence of refraction, and to prevent light passing through the flat part of the plate, the plane surface of the quartz was coated with gold by cathode deposition.

The most striking result derived from the spectral examination of the thirty aerolites is the similarity in composition and the small number of elements which are present. Making due allowance for differences in the photographic activity of the elements in their arc spectra, it is found that only ten of the known elements are present. These elements are iron, chromium, magnesium, nickel, silicon, sodium, manganese, potassium, aluminium, and calcium, and of these, the first four only are present in quantity. Excepting the results for three aerolites, it is found that the relative proportions of the several elements are approximately the same in all. This suggests that the aerolites have a common origin in the disruption of some stellar body for which the process of cosmical evolution is complete. The siderites would appear to have a different origin, or may possibly have formed the solid nucleus or core from which the chromium and other elements have been separated, leaving the magnetic elements iron and nickel as a residue in the familiar ferro-nickel meteorites. H. M. D.

**Hydrogen and Calomel Electrodes.** Gilbert N. Lewis, Thomas B. Brighton, and Reuben L. Sebastian (*J. Amer. Chem. Soc.*, 1917, **39**, 2245—2261. Compare Lewis and Randall, A., 1914, ii, 802).—The results of a number of investigations on (i) the potential of the hydrogen electrode in solutions of hydrochloric acid and potassium hydroxide of various concentrations, (ii) the dissociation constant of water, (iii) the potential of calomel and silver chloride electrodes in solutions of potassium chloride and hydrochloric acid, (iv) methods of establishing definite and reproducible potentials at the boundaries between solutions, and (v) on improvements in the experimental technique of such determinations, are recorded at some length. An electrolytic hydrogen generator which supplies a continuous stream of pure dry hydrogen is described. Electrodes of gold coated with a layer of iridium are recommended as the most suitable for measuring hydrogen ion potentials, since they very rapidly acquire the correct potential and then remain constant. Pieces of apparatus are described in which the hydrogen, calomel, and silver chloride electrodes are most conveniently and accurately built up. A device for maintaining a constant and easily reproducible surface of contact between two liquids is also described. All measurements were made at 25°, and the following results, each the mean of many experiments, are given in the paper:

1. $\mathrm{Hg,HgCl,KCl}\ 0{\cdot}1M \| N.E.$; $e = -0{\cdot}0529$ volt.
2. $\mathrm{Hg,HgCl,HCl}\ 0{\cdot}1M \| \mathrm{KCl}\ 0{\cdot}1M,\mathrm{HgCl,Hg}$; $e = 0{\cdot}0278$ volt.
3. $\mathrm{Ag,AgCl,HCl}\ 0{\cdot}1M \| \mathrm{KCl}\ 0{\cdot}1M,\ \mathrm{AgCl,Ag}$; $e = 0{\cdot}0278$ volt.
4. $\mathrm{Ag,AgCl,HCl}\ 0{\cdot}01M \| \mathrm{KCl}\ 0{\cdot}01M,\ \mathrm{AgCl,Ag}$; $e = 0{\cdot}0272$ volt.

The values of the *E.M.F.* in 2, 3, and 4 afford very good confirmation of the validity of the formula of Lewis and Sargent (A., 1909, ii, 369) for calculating the potential difference between liquid surfaces.

5. $\mathrm{H_2,HCl}\ 0{\cdot}1M,\ \mathrm{HgCl,Hg}$; $e = 0{\cdot}3989$ volt.
6. $\mathrm{H_2,HCl}\ 0{\cdot}1M \| \mathrm{KCl}\ 0{\cdot}1M,\ \mathrm{HgCl,Hg}$; $e = 0{\cdot}4267$ volt.

The value 0·4267 found for the combination 6 can be obtained by calculation from the experimental values of combinations 5 and 2.

7. $\mathrm{H_2,HCl}\ 0{\cdot}01M,\ \mathrm{HgCl,Hg}$; $e = 0{\cdot}5105$ volt. If this value is combined with that obtained from combination 8, the value of the combination 9 can be calculated.
8. $\mathrm{Hg,HgCl,HCl}\ 0{\cdot}01M \| \mathrm{KCl}\ 0{\cdot}01M,\ \mathrm{HgCl,Hg}$; $e = 0{\cdot}0272$ volt.
9. $\mathrm{H_2,HCl}\ 0{\cdot}01M \| \mathrm{KCl}\ 0{\cdot}01M,\ \mathrm{HgCl,Hg}$; $e = 0{\cdot}5377$ volt.

The difference between the *E.M.F.* of cells 5 and 7, that is 0·1116 volt multiplied by $F'$ (23074), gives the free energy of dilution of hydrochloric acid, which equals 2573 cals. From this value, the degree of ionisation of 0·1*M*, 0·03*M*, and 0·01*M* potassium chloride is found to be respectively $\alpha = 0{\cdot}780$, 0·865, and 0·930.

Making use of the foregoing potential values, the value of the *E.M.F.* of the normal calomel electrode is calculated in terms of the value of the normal hydrogen electrode. The following values are obtained:

(*a*) $\mathrm{Hg,HgCl,HCl}\ 0{\cdot}1M \| \mathrm{KCl}\ 0{\cdot}1M,\ \mathrm{HgCl,Hg}$; $e = 0{\cdot}0012$ volt.
(*b*) $\mathrm{H_2,H^{\cdot}}(M) \| \mathrm{HCl},\ 0{\cdot}01M,\ \mathrm{H_2}$; $e = -0{\cdot}0644$ volt.
(*c*) $\mathrm{H_2,H^{\cdot}}(M) \| N.E.$; $e = 0{\cdot}2828$ volt.

In all cases (*a*), (*b*), and (*c*), the contact potential is eliminated. Consequently, if the potential of the normal hydrogen electrode is taken as zero, the potential of the normal calomel electrode is $-0{\cdot}2828$ volt.

10. $H_2$,KOH 0·1*M*||KCl 0·1*M*, HgCl,Hg; $e=1{\cdot}0833$ volts.

11. $H_2$,KOH 0·01*M*||KCl 0·01*M*, HgCl,Hg; $e=1{\cdot}0820$ volts.

The dissociation constant of water is calculated from the hypothetical combination $H_2,OH'(M)||H^{\cdot}(M)H_2$; $e=0{\cdot}8278$ volt, and the value $K_w=1{\cdot}012\times10^{-14}$ obtained. It is shown that the values of the *E.M.F.* obtained when the gas pressure is changed do not vary more than 0·00001 volt from the values calculated from the thermodynamic equation. J. F. S.

**Free Energy of Hydrochloric Acid in Aqueous Solution. II.** ARTHUR A. NOYES and JAMES H. ELLIS (*J. Amer. Chem. Soc.*, 1917, **39**, 2532—2544. Compare A., 1916, ii, 369).—In continuation of previous measurements of the *E.M.F.* of cells of the type $H_2|HCl|HgCl|Hg$, the authors have replaced the calomel electrode by a silver chloride electrode with the object of obtaining more accurate data for acid solutions of low concentration. Data are recorded for solutions varying in concentration from 0·3 to 0·001*N* at 15°, 25°, and 35°. The changes in the free energy and total energy attending the transfer of one gram-molecule of hydrogen chloride from solutions of varying concentration to a 0·1*N*-solution are calculated from the data, and it is inferred that hydrochloric acid is by no means completely ionised in 0·003*N*-solution.

On the assumption that the ionic activity and the ionic concentration can be regarded as equal in the case of this dilute solution, the authors have recalculated the activity coefficients for hydrochloric acid in solutions varying in concentration from 0·003 to 4·5*N*. As before (*loc. cit.*), these activity coefficients are found to diverge from the conductivity ratio $\Lambda/\Lambda_\infty$ by about 10% in the case of a 0·1*N*-solution. The calculated activity coefficients diminish with increase in the concentration of the acid up to 0·5*N*, but increase rapidly as the concentration of the acid is further increased. H. M. D.

**Potential of the Bromine Electrode: Free Energy of Dilution of Hydrogen Bromide: Distribution of Bromine between Several Phases.** GILBERT N. LEWIS and HYMAN STORCH (*J. Amer. Chem. Soc.*, 1917, **39**, 2544—2554).—A platinum iridium electrode immersed in a solution of potassium bromide or hydrobromic acid containing free bromine has been used in the determination of the potential of the bromine electrode by measurements of the *E.M.F.* of the cells obtained by combination of this with the calomel or the hydrogen electrode. The acid cell affords the more trustworthy results, and the value of the bromine potential for a solution containing bromine and bromide ion in molar concentration against the normal hydrogen electrode is found to be $-1{\cdot}0872$ volts.

By measuring the *E.M.F.* of the cell $H_2|HBr|AgBr|Ag$ for HBr concentrations equal to 0·01, 0·03, and 0·1*N*, it has been found that the ionic activity coefficients are very nearly equal to those previously found for HCl at the same concentrations.

The determination of the ratio of distribution of bromine between carbon tetrachloride and aqueous solutions of 0·001*N*- and 0·1*N*-hydrobromic acid has shown that the constant

$$K=[HBr_3]/[HBr][Br_2]$$

has nearly the same value as the constant for a solution in which the hydrobromic acid is replaced by potassium bromide.

By passing a current of dry air through solutions of bromine in carbon tetrachloride, it has been found that the vapour pressure of the bromine is proportional to the concentration of the solution when this is measured in terms of molar fractions. H. M. D.

**Ionisation and Polymerisation in Cadmium Iodide Solutions.** R. G. Van Name and W. G. Brown (*Amer. J. Sci.*, 1917, [iv], **44**, 453—468. Compare A., 1917, ii, 455).—In the further investigation of the constitution of cadmium iodide solutions, measurements have been made of the *E.M.F.* of cells in which iodine electrodes are in contact with iodine–cadmium iodide solutions, and also of the freezing points of solutions containing cadmium iodide and varying proportions of iodine.

The freezing-point data show that the freezing point of a cadmium iodide solution is depressed to the extent of about 1·4° per mol. of added iodine. This lowering is very nearly the same for solutions in which the cadmium iodide concentration is varied considerably. The facts point to the existence of polymerised molecules in considerable quantity.

From the *E.M.F.* data it is possible to calculate the iodine ion concentration in iodine–cadmium iodide solutions, and by extrapolation to zero iodine concentration to obtain the iodine ion concentration for pure solutions of cadmium iodide. For the more dilute cadmium iodide solutions examined (0·01 and 0·125 molar) the data are in agreement with the assumption that complex molecules are present, but the behaviour of the stronger solutions does not appear to be compatible with this hypothesis.

The assumption that complex molecules of the type $(CdI_2)_3$ are the only complex molecules formed is found to be insufficient to reconcile the observations which have been made according to the distribution, freezing-point, and *E.M.F.* methods. H. M. D.

**A Comparison of the Activities of Two Typical Electrolytes.** G. A. Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 2601—2605).—Measurements of the *E.M.F.* of cells of the type $H_2|HCl|HgCl|Hg$ have been made for solutions containing from 0·01 to 16·0 mols. of hydrogen chloride in 1000 grams of water. From the results, the ionic activities are calculated and compared with the corresponding values for potassium chloride. On the assumption that these thermodynamic quantities afford a measure of the degree of ionisation of the two electrolytes, it is found that there is a considerable divergence between the degrees of ionisation even in dilute solution, whilst in concentrated solutions the divergence is enormous. H. M. D.

**Specific Heats and Heats of Fusion of Triphenylmethane, Anthraquinone, and Anthracene.** JOEL H. HILDEBRAND, (MISS) ALICE D. DUSCHAK, A. H. FOSTER, and C. W. BEEBE (*J. Amer. Chem. Soc.*, 1917, **39**, 2293—2297).—The specific heat and latent heat of fusion of triphenylmethane, anthraquinone, and anthracene have been determined in a calorimeter similar to that described by Lewis and Randall (A., 1911, ii, 371). The specific heats were determined over several temperature ranges. The materials were contained in vessels of quartz glass or "pyrex" glass, and consequently the specific heat of these substances had to be determined. The following values were obtained: pyrex glass, $s=0·174+0·00036t$; quartz glass, mean value over the range 20—320°, $s=0·2161$; triphenylmethane, solid, $s=0·186+0·00277t$, liquid, $s=0·479$; anthraquinone, solid, $s=0·258+0·0007t$, liquid, $s=0·66$; anthracene, solid, $s=0·280+0·0007t$, liquid, $s=0·509$. The following heats of fusion were also obtained: triphenylmethane, 17·8 cal.; anthraquinone, 37·4 cal.; anthracene, 38·7 cal. It is pointed out that the specific heat equation for triphenylmethane is not trustworthy for extrapolation to lower temperatures, as the range of temperature from which it was obtained was so small (20—60°), and it is also suggested that the temperature coefficient of the specific heat is much larger than would be expected.

J. F. S.

**The Entropy of the Elements and the Third Law of Thermodynamics.** GILBERT N. LEWIS and G. E. GIBSON (*J. Amer. Chem. Soc.*, 1917, **39**, 2554—2581).—A theoretical paper in which the authors have calculated the entropies of the elements and applied the results in testing the theorem of Nernst, which may be regarded as equivalent to the statement that the entropy of every substance is zero at the absolute zero of temperature. On the assumption that the entropy of a substance is known at one temperature, the entropy at any other temperature can be calculated if the specific heat is known for the interval of temperature concerned. It is shown that the entropy may be calculated by a graphical method which does not necessitate any assumption in regard to the exact form of the heat capacity equation. The calculated atomic entropies show with respect to atomic weight or atomic number the same kind of periodicity which characterises certain other properties of the elements.

According to the equation $\Delta F-\Delta H=-T\Delta S$, in which $\Delta F$ is the increase in free energy, $\Delta H$ the increase in total energy, and $\Delta S$ the increase in entropy for any isothermal change, it is possible to calculate the free energy of formation of any compound from its elements if the entropies of the compound and of the elements and the heat of formation of the compound are known. Conversely, the entropy change associated with the formation of a compound from its elements can be calculated from the equation if the changes in total and free energy are known.

The entropy differences, thus calculated, for a number of compound substances are found to agree satisfactorily with those which are derived from the atomic and molecular entropies, calculated according to the method referred to above, in which it is assumed that the entropies of the elements and compounds are zero at the absolute zero of temperature.

This agreement is considered to afford new support for the so-called third law of thermodynamics. H. M. D.

**Determination of Boiling Points in Capillary Tubes.** Friedrich Emich (*Monatsh.*, 1917, **38**, 219—223).—An open glass tube 7—8 cm. long, of external diameter 0·6—1·2 mm., and with a wall 0·1 mm. thick, is drawn out at one end to a fine capillary approximately 2 cm. long and of 0·05—0·1 mm. diameter. The end of the capillary is immersed in the liquid to be examined, and when about half a cubic millimetre has entered, the tip is sealed by contact with a flame. If this operation is successful, the capillary will have a minute bubble at the extreme end covered by a liquid plug nearly 1 millimetre in length. The tube is attached to a thermometer and warmed in a bath in which the heating liquid is 4—5 cm. deep. As the temperature is raised, the plug of liquid ascends the capillary, and the b. p. is registered when the plug reaches the level of the surface of the heating liquid outside. The method is, naturally, restricted to pure substances.

D. F. T.

**An Efficient Apparatus for Fractional Distillation under Diminished Pressure.** William A. Noyes and Glenn S. Skinner (*J. Amer. Chem. Soc.*, 1917, **39**, 2718—2720).—A modified Claisen flask is used. The side-tube of the flask is bent upwards and fused on to a simple fractionating column, and into the side of the neck of the flask is fused a separating funnel. The flask can thus be used for large or small fractions by regulating the flow of liquid from the separating funnel, and successive fractions may be introduced without losing the vacuum. W. G.

**Studies in Catalysis. VIII. Thermochemical Data and the Quantum Theory. High Temperature Reactions.** William Cudmore McCullagh Lewis (T., 1917, **111**, 1086—1102. Compare *ibid.*, 457).—According to the radiation theory and the quantum hypothesis, the heat of a reaction $Q$ is given by the equation $Q = Nh(\Sigma\nu_2 - \Sigma\nu_1)$, in which $N$ is the Avogadro constant, $h$ the Planck constant, $\Sigma\nu_1$ the sum of the critical frequencies of the reacting substances, and $\Sigma\nu_2$ the corresponding quantity for the resultant products. This relation has been previously deduced by Haber (*Ber. Deut. physikal. Ges.*, 1911, **13**, 1117), who calculated the critical frequencies of substances for which the requisite data were not available by means of the semi-empirical relation $\nu_v/\nu_r = \sqrt{M/m}$, in which $\nu_v$ is the characteristic ultra-violet frequency, $\nu_r$ the characteristic ultra-red frequency in terms of which the specific heat may be represented, $M$ the molecular weight of the substance, and $m$ the mass of an electron. The use of this equation involves considerable uncertainty in regard to $M$, and in Haber's treatment of the problem in its application to the formation of a salt, such as sodium chloride, from its elements, the quantity $\Sigma\nu_1$ is arbitrarily made equal to half the sum of the critical frequencies of the elements instead of the entire sum.

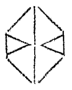
By making the assumption that the ultra-violet quantum breaks the bond between two adjacent atoms, which are both thereby rendered chemically active, it follows that one quantum characteristic of sodium plus one quantum characteristic of chlorine will suffice to bring about the change represented by $2Na + 2Cl = 2NaCl$. Hence, $2Nh\nu_{NaCl} - Nh(\nu_{Na} + \nu_{Cl})$ should be equal to the heat of formation of two gram-molecules of sodium chloride. This relation is identical with that which follows from the introduction of the arbitrary assumption which is characteristic of Haber's method of treatment.

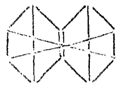
The application of the equation to the calculation of the heat of formation of sodium chloride may be briefly indicated. From the wave-length ($\lambda = 52\,\mu$) of the characteristic infra-red band, $\nu_r = 0{\cdot}0577 \times 10^{14}$. By means of the square root relation (see above), $\nu_v = 19{\cdot}27 \times 10^{14}$, from which the critical increment $Nh\nu_{NaCl} = 182{,}290$ cal. Similarly, the sum of the critical increments for 1 gram atom of sodium and 1 gram atom of chlorine is found to be 85,000 cal. The heat of formation of the salt is therefore $182{,}290 - 85{,}000 = 97{,}290$ cal., which agrees with the observed value, 97,800 cal.

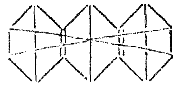
Similar calculations have been made in respect of other substances for which the requisite data are available, and the results, when compared with the observed heats of reaction, show a degree of agreement which supports the validity of the equation connecting the heat of reaction and the critical frequencies. H. M. D.

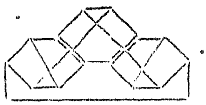
**Thermochemical Studies.** DANIEL LAGERLÖF (*J. pr. Chem.*, 1917, [ii], **96**, 26—34).—A theoretical paper in extension of the earlier mathematical discussion (A., 1904, ii, 382, 605; 1905, ii, 76, 677) of the heat of formation of carbon compounds, the thermal effect of the intramolecular linkings being especially considered from the author's point of view. D. F. T.

**Thermochemical Studies. The Constitution of Benzene and of some Condensed Aromatic Hydrocarbons considered from the Thermochemical Point of View.** DANIEL LAGERLÖF (*J. pr. Chem.*, 1917, [ii], **96**, 35—49).—The relative stability of the cyclic hydrocarbons, containing rings larger than *cyclo*pentane as compared with the smaller rings such as *cyclo*propane, is attributed to the strain in reducing the angle between the carbon valencies in the latter causing an endothermic effect, whereas, in the author's view, the enlarging of the valency angle in the formation of hexatomic and bigger rings produces an exothermic effect if the ring is a plane one. Mathematical arguments are adduced in favour of this theory, and the annexed formulæ are suggested for benzene, naphthalene, anthracene, and phenanthrene respectively.









D. F. T.

**The Standard Unit in the Thermochemistry of Organic Compounds.** W. SWIENTOSLAWSKI (*J. Amer. Chem. Soc.*, 1917, **39**, 2595—2600).—The values obtained for the heats of combustion of naphthalene, benzoic acid, and sucrose in recent measurements are compared and discussed. In terms of the 15° calorie, the most probable values for the heat of combustion of 1 gram of substance, weighed in air, are: naphthalene, 9612 Cal.; benzoic acid, 6311 Cal.; sucrose, 3945 Cal.

To obtain satisfactory agreement in thermochemical data, it is recommended that the heat capacity of calorimetric bombs should be determined by a standard method involving the use of a standard combustible substance. The question whether the heat of combustion is to be expressed in terms of kilo-joules or calories should be determined by the International Congress. Until the standard substance has been decided on, the calibration of calorimetric bombs should be based on one or other of the above values for the heats of combustion of naphthalene, benzoic acid, or sucrose.

H. M. D.

**Improved Form of Pyknometer.** MARKS NEIDLE (*J. Amer. Chem. Soc.*, 1917, **39**, 2387—2388).—A modification in the cap of the side arm of a pyknometer to provide for any liquid which may be driven out of the instrument by expansion during the weighing.

J. F. S.

**Improved Victor Meyer Vapour Density Apparatus.** D. A. MACINNES and R. G. KREILING (*J. Amer. Chem. Soc.*, 1917, **39**, 2350—2354).—Improvements to the Victor Meyer vapour density apparatus in connexion (i) with the means of introducing the substance, (ii) with the vaporisation tube, are described. It is pointed out that when the cork of the usual form of the apparatus is withdrawn to allow of the admission of the substance under investigation, there is a certain amount of cooling of the air inside the tube, also there may be a certain amount of spirting of the liquid on to the walls of the vaporisation tube. Both these effects will produce errors. The authors suggest a means of introducing the substance at the bottom of the bulb, and at the temperature of the vaporisation tube. A long glass tube reaching almost to the bottom of the vaporisation tube is fitted by means of a rubber stopper in the neck of the apparatus. A brass rod, fitted with a hook at its lower end, passes down this tube and is made air-tight at the upper end by means of a rubber tube. The substance under investigation is placed in a small bulb which has a long capillary neck (2—3 cm.) bent twice at right angles. This is placed on the brass hook and the rod drawn up until the bulb neck just touches the enclosing glass tube. When the temperature of the vaporisation vessel is constant, the bulb is broken by drawing the brass rod slightly further up the tube.

It is stated that the air in the ordinary vaporisation tube not being all at the same temperature is the cause of many errors. To obviate these, the authors suggest a modified form of vaporisation vessel. This consists of a large test-tube 25 cm. long and 5 cm. diameter, which carries a rubber stopper, through which passes a capillary delivery tube and a straight tube 28 cm. long and 1·5 cm. diameter. The latter tube is placed centrally, reaches almost to the bottom of the outer vessel, and carries the breaking apparatus described above. The whole apparatus is placed in a large boiling tube in the usual manner. It is to be pointed out that with this apparatus, owing to the sudden rush of air when the tube of material is broken, the usual eudiometer and pneumatic trough are useless, and must be replaced by a gas burette. Trial experiments are described with numerical details for bromine, ethyl alcohol, and diethyl ether. The results are in every way quite good.

J. F. S.

**Convergence of the Liquid and Solid Volume Curves to Absolute Zero.** Gervaise Le Bas (*Chem. News*, 1917, **116**, 307—308).—It is shown that, in general, the solid and liquid curves converge to absolute zero. This applies to types of substances where the liquid volume curve is steeper than the solid curve, where the volume of the resultant solid is greater than that of the liquid.

W. P. S.

**The Relation between Temperature and Molecular Surface Energy for Liquids between −80° and 1650°.** F. M. Jaeger (*Zeitsch. anorg. Chem.*, 1917, **101**, 1—214).—The author has determined the surface tension and molecular surface energy of about 200 organic liquids between −80° and 250°, and of about 50 inorganic substances in the molten condition between 300° and 1650°. The method employed was to determine the bursting pressure of bubbles of the liquid blown on the end of a capillary tube of known diameter just immersed in the liquid. For high-temperature work, the substance under examination was melted in a vessel of platinum or platinum–rhodium heated in a resistance furnace, the capillary tube being of the same material. The complicated apparatus used is described and illustrated in great detail.

In the specially designed manometer, normal octane was used in contact with mercury; it is strongly recommended as an ideal liquid for this purpose.

For each of the substances examined a table is given, in which is detailed, for each temperature at which observations were made, (1) the surface tension $\chi$ in ergs per square centimetre, calculated from the equation $\chi = rH/2$, where $r$ is the radius of the capillary and $H$ is the bursting pressure in dynes; (2) the density, $d$, of the liquid; (3) the molecular surface energy $\mu$ in ergs per square centimetre, where $\mu = \chi(M/D)^{\frac{2}{3}}$; (4) the specific cohesion $A^2 = 2\chi/(g \cdot d)$; (5) the quantity $(A^2M)/T$, where $T$ is the absolute temperature of the melting point; (6) the temperature coefficient of the molecular surface energy, $d\mu/dt$. Every substance examined was carefully purified and its density determined at different temperatures, special methods being developed for the high-temperature measurements. For many of the substances $\chi$-$t$ and $\mu$-$t$ curves are given.

It has been demonstrated by Eötvös, from van der Waals's law of corresponding states, that for normal, non-associated liquids $d\mu/dt$ should be a constant $= 2{\cdot}25$ ergs per 1°, whilst for associated liquids the temperature coefficient should be smaller. Further, it can be shown thermodynamically that if $d\mu/dt$ is a constant, the specific heat of the surface layer must be the same as that of the bulk of the liquid.

The great number of $\mu$-$t$ curves now examined illustrates well the constitutive character of molecular surface energy. The curves are rarely straight lines, the value of the temperature coefficient, in the case of organic liquids, generally falling, but sometimes increasing, with rising temperature. In general, in a series of related substances, such as alcohols, fatty acids, or esters, at a given temperature, the value of $\mu$ increases with the molecular weight. The introduction of increasing quantities of halogen into hydrocarbons also increases the molecular surface energy. Isomeric substances, such as ethylene dichloride and ethylidene chloride, show wide differences. The value of $d\mu/dt$ is fairly constant for a series of related substances, but marked exceptions sometimes occur; thus formic acid has an exceptionally low value. In the primary, secondary, and tertiary aliphatic amines, the values of $\mu$ and $d\mu/dt$ increase very markedly with increasing carbon content, the lower members of the series having abnormally low temperature coefficients. Of isomeric primary amines, those with straight carbon chains have greater molecular surface energy than those with branched chains. Unsaturated substances, such as allylamine, have higher values of $\mu$ than the corresponding saturated compounds. Formamide has an exceptionally low temperature coefficient, 0·89 erg per 1°, similar to that of water. This fact is probably to be associated with its high dissociating power.

The unsaturated character of aromatic compounds is accompanied by increased values of $\mu$. The halogenated compounds show increasing values of $\mu$ with increasing molecular weight. Position isomerides show marked differences; for example, of the three nitrophenols, the para-compound has the greatest and the ortho-compound the least molecular surface energy. In the nitroanisoles the differences are much less marked, probably because here there is no mobile hydrogen atom. The molecular surface energy of aniline and its homologues is much higher than that of any of the primary aliphatic amines up to heptylamine. The introduction of halogen or nitro-groups into aniline increases the value of $\mu$, as in the hydrocarbons. The surface energy relationships of many other aromatic compounds are discussed.

Specially interesting are the $\mu$-$t$ curves for such substances as *p*-azoxyanisole, *p*-azoxyphenetole, and anisaldazine, which form anisotropic liquids (liquid crystals). The curve consists of two distinct portions with a sharp minimum where the liquid passes from the anisotropic to the normal form. The temperature coefficient of the anisotropic liquid is always greater than that of the normal liquid, a fact which is contrary to Eötvös's conclusion that a lower temperature coefficient indicates a greater degree of molecular association. It is concluded that in substances of this class, very complex and little understood changes are brought about by heat.

The relationships among the haloids of phosphorus, arsenic, antimony, and bismuth are in general similar to those among organic halogen compounds, the values of $\chi$ and $\mu$ increasing with the molecular weight, whilst the magnitude of $d\mu/dt$ is more or less normal. Quite different, however, are the haloids of the alkali metals lithium, sodium, potassium, rubidium, and cæsium. For the same metal, the surface tension $\chi$ of the molten salt decreases with increasing atomic weight of the halogen from fluorine to iodine, and also decreases, for the same halogen, with increasing atomic weight of the metal. The values of $\mu$ vary in an irregular manner, whilst $d\mu/dt$ is in all cases abnormally small. Other salts investigated include sulphates, nitrates, borates, molybdates, and tungstates of the alkali metals.

It is concluded that at high temperatures the law of corresponding states cannot hold for molten salts, which are probably highly ionised, and that Eötvös's rule, based on the validity of this assumption, that a low value of $d\mu/dt$ indicates a high degree of association in the liquid, is therefore invalid. Also, since $d\mu/dt$ is by no means constant for organic or inorganic liquids, the specific heat of the surface layer must be different from that of the rest of the liquid, and the surface energy must be, at least in part, of a kinetic nature.

The author has investigated the empirical rule, discovered by Walden, that for many non-associated liquids the quotient obtained by dividing the molecular cohesion by the absolute temperature of (*a*) the melting point or (*b*) the boiling point is a constant, in the case of (*a*) 3·65 and of (*b*) 1·15 approx. The values of these two "constants" have been calculated and tabulated by the author for about 200 different substances, which are divided into four groups according to the manner in which either value varies from the mean. The rule is evidently only approximate, and many variations occur which cannot be explained on the ground of molecular association. The greatest irregularities occur, however, among inorganic salts. E. H. R.

**Solubility and Internal Pressure.** JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1917, **39**, 2297—2301. Compare A., 1916, ii, 518).—Where Raoult's law is obeyed by a solution, the solubility of the solid at the absolute temperature $T$ may be calculated by means of the expression $\log N = -LTT_m/4{\cdot}58(T_m - T)$, where $N$ is the solubility expressed in terms of molecular fractions, $L$ is the molecular heat of fusion, and $T_m$ the melting point in absolute degrees. The author has calculated the solubility of anthracene, anthraquinone, *p*-dibromobenzene, phenanthrene, and triphenylmethane at 25° by means of the formula, and compared these values with the experimentally determined solubilities (see this vol., i, 62) in some eight solvents. Iodine has been treated similarly. The divergence of the solubility from the calculated value is considered along with the internal pressure of the solvent, and it is shown in the case of anthracene, which has practically the calculated solubility in carbon disulphide, that its solubility decreases with decreasing internal pressure for non-polar liquids. In the case of alcohol, a polar liquid, the divergence from the calculated solubility is much greater, a fact which agrees with the third rule previously stated (*loc. cit.*). J. F. S.

**Formation of Additive Compounds in Aqueous Solutions. Stability of Hydrates and the Determination of Hydration in Solution.** JAMES KENDALL, JAMES ELIOT BOOGE, and JAMES C. ANDREWS (*J. Amer. Chem. Soc.*, 1917, **39**, 2303—2323).—The results of previous work on the formation of additive compounds are summarised, and the general rules established in this work are recapitulated and extended to aqueous solution (A., 1914, i, 858, 1069; 1915, i, 15, 80; 1916, i, 599, 707). Since water can function both as a weak acid and a weak base, the extent of hydration in aqueous solutions should be found to increase with the increasing acidity or basicity of the solute. The known hydrates of acids and bases are reviewed in the paper, and it is shown that only the stronger acids and bases yield compounds with water which are capable of isolation. A number of freezing-point determinations with solutions of varying concentrations of the following acids, acetic, β-hydroxypropionic, α-hydroxypropionic, citric, *d*-tartaric, hydrofluoric, phosphoric, and hydrochloric, have been carried out. The results in all cases conform exactly with the above-mentioned prediction. A critical discussion is given of the factors which must be taken into consideration in the determination of hydration in solution by the freezing-point method. The question of the hydration of salts is treated in a preliminary manner, and it is shown that the hydration follows the order of the scheme

$$Ce < Rb < K < NH_4 < Na < Li$$

and $NO_3 < Cl < Br < I$. J. F. S.

**Mechanism of the Ionisation Process.** JAMES KENDALL and JAMES ELIOT BOOGE (*J. Amer. Chem. Soc.*, 1917, **39**, 2323—2333).—The results of a number of papers by the authors (see preceding abstract) have indicated an intimate and general connexion between ionisation and the formation of compounds in solution. In the present paper the authors advance the hypothesis that ionisation is preceded by combination between solvent and solute, and is, indeed, a consequence of such combination. This point of view combines the current ionic and hydrate hypotheses, referring conductivity in solutions to the dissociation of solute–solvent complexes into radicles of opposite charge. The actual mechanism of the ionisation process under this assumption, with its relation to phenomena such as unsaturation, association, and high dielectric constant, is briefly discussed. It is shown that compound formation between solvent and solute may be postulated in all conducting solutions, and that the distinction still commonly retained between the two components is arbitrary and misleading. The general evidence in favour of the hypothesis is given in a preliminary form, attention being centred on a few fundamental points only. J. F. S.

**Soap Bubbles as Models of Crystal Structure.** M. J. MARSHALL (*J. Amer. Chem. Soc.*, 1917, **39**, 2386—2387).—It is shown that when small soap bubbles of uniform size are produced on the surface of a soap solution, they form a symmetrical network which is in reality the simple face-centred lattice as found in crystals of pure metals. These bubble aggregates can readily be produced and projected on the screen, and so serve to show causes of crystal structure and the method of building up of crystals. The best effects are produced by using a solution of sodium oleate to which glycerol has been added, and blowing the bubbles by means of a glass tube which has been constricted to 1 mm. diameter by drawing, and then further constricted to a very fine tip by allowing the walls of the 1 mm. tube to fall together in a smoky flame. The jet should be at right angles to the surface of the soap solution when the bubbles are blown. J. F. S.

**Formation of Crystals in Gels.** HARRY N. HOLMES (*J. Physical Chem.*, 1917, **21**, 709—733).—The influence of silicic acid gels on the formation of crystals has been examined by experiments in which one of two reacting soluble substances was added to a solution of silicic acid, which was then allowed to set. The second substance, dissolved in water to give a solution having a greater osmotic pressure than the jelly, was then brought into contact with the upper surface of the jelly and slow diffusion allowed to take place. If an insoluble substance is produced by the reaction, this forms within the jelly, and the slow diffusion process leads to the formation of large, well-developed crystals. Perfectly formed tetrahedral crystals of copper may, for instance, be obtained by the diffusion of hydroxylamine hydrochloride into a silicic acid gel containing copper sulphate. Other substances obtained in crystalline form by this method were silver dichromate, gold, lead iodide, mercuric iodide, basic mercuric chloride, silver sulphate, silver acetate, and basic lead chromate.

The capillarity associated with the gel structure is supposed to be partly responsible for the observed crystal growth, and a similar influence is brought into play when the fine-grained precipitation membrane begins to be formed. In support of the theory that the capillary diffusion is the chief factor in the phenomenon, it has been observed that well-formed crystals may be obtained by allowing slow diffusion to take place through flowers of sulphur, barium sulphate, or alundum. H. M. D.

**Properties of Mixed Liquids. III. Law of Mixtures. I.** J. LIVINGSTON R. MORGAN and MARY A. GRIGGS (*J. Amer. Chem. Soc.*, 1917, **39**, 2261—2275. Compare A., 1916, ii, 224, 296).—With the object of testing the validity or otherwise of the simple law of mixtures, the surface tension of a number of homogeneous mixtures has been determined by the drop-weight method at two temperatures in each case. The lower temperature was 10° or 15° and the higher temperature 40°. The following mixtures in a series of compositions were measured: (*a*) Binary mixtures: benzene–toluene, benzene–ethyl propionate, benzene–chlorobenzene, benzene–methyl butyrate, benzene–propyl acetate, benzene–acetone, toluene–ethyl propionate, toluene–chlorobenzene, toluene–methyl propionate, toluene–ethyl formate, acetone–chlorobenzene, chlorobenzene–ethyl propionate, ethyl lactate–propyl acetate, chlorobenzene–methyl butyrate, amyl β-phenylpropionate–methyl propionate, and acetone–propyl acetate. (*b*) Ternary mixtures: benzene–toluene–ethyl propionate, benzene–toluene–chlorobenzene, benzene–toluene–methyl propionate, and benzene–toluene–acetone. (*c*) Quaternary mixtures: benzene–toluene–ethyl propionate–chlorobenzene, benzene–toluene–methyl propionate–ethyl lactate, and benzene–toluene–methyl butyrate–propyl acetate. (*d*) Quinary mixture: benzene–toluene–methyl butyrate–propyl acetate–methyl propionate. It is shown that ten of the above-mentioned mixtures follow rigidly the law of mixtures in the form $P_{Mixt.} = l_aP_a + l_bP_b +$, etc. (where the summation of the relative weights $l_a$, $l_b$, etc., is equal to unity. Of these mixtures, six were of two constituents, two of three constituents, one of four constituents, and one of five constituents. Where variations appear, the observed value is invariably less than that calculated from the law. These deviations increase in magnitude with increased temperature, and are always at a maximum at both temperatures for that mixture which contains equal weights of the constituents. Although the deviations might be due to the magnitude of the difference in the surface tension values of the constituents when pure, the effect is probably negligible and merges into the more important factor—the nature of the constituent. An example of the latter is chlorobenzene, which renders every mixture in which it is present abnormal. The deviation of a complex mixture is not a summation of the deviations of the pairs of liquids of which it could be made, but is of the same order as these. It is further shown that chemical interaction for binary mixtures could not be the cause of the maximum deviation invariably found at a composition of 50% by weight of the two constituents, whereas this behaviour is shown to be exactly what might be expected if the one liquid by its simple, physical presence influenced the value of the property of the other, and the conclusion is consequently drawn that the mixture law considered is a rigid law provided no chemical action takes place between the constituents and neither liquid influences the value of the property of the other. J. F. S.

**Properties of Mixed Liquids. IV. Law of Mixtures. II.** J. Livingston R. Morgan and Andrew J. Scarlett, jun. (*J. Amer. Chem. Soc.*, 1917, **39**, 2275—2293. Compare preceding abstract).—The surface tension of the following binary mixtures, (i) water–acetone, (ii) acetone–ethyl alcohol, (iii) phenol–acetone, (iv) phenol–ethyl alcohol, (v) benzene–acetic acid, (vi) benzene–ethyl alcohol, (vii) benzene–methyl alcohol, (viii) acetone–methyl alcohol, (ix) ethyl alcohol–methyl alcohol, and (x) benzene–phenol, has been determined by the drop-weight method over a range of concentrations and temperatures. The curves representing the variation in surface tension with concentration are in general without maxima or minima, but that of (v) shows a minimum, whilst (ii) and (viii) show maxima. The comparison of the experimental results with those calculated by means of the mixture law of Morgan and Griggs leads to the following observations, which fall into three groups: (*a*) the systems (i), (iii), (iv), (v), (vi), (vii), and (x) give values smaller than the calculated values; (*b*) systems (ii) and (viii) give values larger than the calculated values; (*c*) the remaining system, (ix), gives a slight positive deviation at 0°, no deviation at 30°, and a slight negative deviation at 45°.

The position and magnitude of the maximum deviation, from the mixture law, found when the deviation is plotted against the concentration of one constituent, divides the systems into two classes. In one class the maximum deviation, always very small, is found for a mixture containing 50% by weight of each constituent. The systems falling into this group are (ii), (viii), and (ix). The only explanation of this behaviour is that it is due to the physical effect of the one liquid on the other, since an equal weight of the two constituents brings about the effect.

Systems of the other class, on the contrary, exhibit a maximum deviation, usually large, and at some other concentration than 50% which corresponds always with some simple and even relation of the molecular weights of the constituents, that is, corresponds with a definite chemical formula. The cause of this, according to the theory put forward by Denison (A., 1913, ii, 30), is the actual production of a compound. The molecular compounds found to exist in the binary mixtures of liquids examined are: $COMe_2,10H_2O$, $2PhOH,COMe_2$, $PhOH,2EtOH$, $C_6H_6,2CH_3{\cdot}CO_2H$,

$2C_6H_6$,EtOH, $C_6H_6$,MeOH, and 4PhOH,$3C_6H_6$. The existence of these compounds in solution is confirmed by density and viscosity measurements. The compound $C_6H_6,2CH_3\cdot CO_2H$ shown to exist in the system benzene–acetic acid is particularly interesting when considered in the light of the results of other methods, which lead to the conclusion that acetic acid is always polymerised into double molecules in benzene solution. These methods are such, however, as would fail to show a combination of the solvent with the polymerised solute, even if it did exist; and hence the evidence found here is not only not inconsistent with other evidence, but gives a wider point of view on the process which has been designated hitherto as a simple polymerisation. J. F. S.

**System of Recording Rate of Chemical Reaction.** JAMES W. McBAIN (*Chem. News*, 1917, **116**, 315—316).—It is suggested that the usual expression for denoting the velocity constant of a reaction may be replaced by a number which has a direct physical significance. For instance, it may be written $k=1/t$ (remainder of the expression), where $k$ is the present rate constant of the reaction and $t$ is the time the reaction has proceeded, or $kt=$ (remainder of the expression). It is necessary to give the value of $k$ and also the value of the unit of time (minutes or hours). The value of $k$ is, however, always set at unity, and the unit of time is chosen accordingly; the equation then becomes $t=$ (remainder of the expression). The chief advantage is that the proposed "unit of time" gives a direct idea of the rate of the reaction. W. P. S.

**Contact Catalysis. III.** WILDER D. BANCROFT (*J. Physical Chem.*, 1917, **21**, 734—775. Compare A., 1917, ii, 566; this vol., ii, 13).—A review of the literature relating to the action of poisons in contact catalytic reactions. The changes in over-voltage produced by certain ions are supposed to be effects which are comparable with retarded or inhibited contact catalytic reactions.

H. M. D.

**Revision of Atomic Weights in 1916.** E. MOLES (*J. Chim. phys.*, 1917, **15**, 433—469).—A review of the work on the determination of atomic weights published during 1916. H. M. D.

**Errors affecting the Determination of Atomic Weights. VI. Surface Actions as a Source of Errors in Weighing.** PH. A. GUYE and E. MOLES (*J. Chim. phys.*, 1917, **15**, 360—404. Compare A., 1916, ii, 385, 386, 432, 445).—A further consideration of the errors involved in the accurate determination of equivalent weights, in which the authors direct attention to the anomaly, first pointed out by Hinrichs (compare A., 1893, ii, 163, 316; 1894, ii, 276), that the value of the combining ratio is a function of the quantity of substance used in the determinations. It is considered that the available data afford clear evidence that such a relation does actually exist, but the interpretation given by Hinrichs is considered to be unacceptable

By reference to data obtained in recent work on the determination of atomic weights, it is found that all series of measurements do not show the occurrence of such a connexion between the combining ratio and the quantity of substance operated on, but that this is confined to series of determinations in which the quantities of substance employed have been determined by weighing in air, the reduction to a vacuum being effected by calculation. This suggests that the anomaly is due to surface condensation of air, water, etc., and it is shown that the curves which express the relation between the experimental combining ratio and the weight of substance operated on can be satisfactorily accounted for on this hypothesis. The average relative deviation attributable to this source of error is 1 in 20,000, but it is sometimes as high as 1 in 10,000. H. M. D.

**Errors affecting the Determination of Atomic Weights. VII. Surface Actions as a Source of Errors in Weighing.** Ph. A. Guye and E. Moles (*J. Chim. phys.*, 1917, **15**, 405—432. Compare preceding abstract).—Experiments have been made with silver in the form of a solid block and with finely powdered zinc oxide with the object of ascertaining the magnitude of the errors which may be ascribed to the formation of a surface film when these substances are weighed in the air. In the case of silver, the error involved amounts to $2 \times 10^{-5}$ gram per gram of silver. This value is to be regarded as a minimum, the actual error in practice depending on the humidity of the air in the balance case, on the nature of the surface of the metal, and on other factors. The error attributable to surface condensation, according to the experiments with zinc oxide, is of the order $0{\cdot}2$ to $0{\cdot}4 \times 10^{-5}$ gram per gram of substance.

It is shown that errors of this order of magnitude affect the value of the second decimal figure when the atomic weight of the element under consideration is greater than 100. The errors in question should be eliminated in atomic weight measurements by actually weighing the substances involved in a vacuum. The possibility of making such weighings has been greatly increased as a result of recent improvements in the technique of various forms of microbalance. H. M. D.

**Graphical Interpolation of Tabulated Data.** Horace G. Deming (*J. Amer. Chem. Soc.*, 1917, **39**, 2388—2392).—A method is described, based on the principle of a triple parallel alignment chart, whereby the interpolated values required from data may be rapidly obtained by a graphic method. It is claimed, for example, that the adoption of this principle to logarithm tables would reduce the amount of space occupied by such tables to about 10% of that now necessary. J. F. S.

# Inorganic Chemistry.

**Revision of the Atomic Weight of Bromine. Normal Density of Hydrogen Bromide Gas.** CLARENCE KENWORTHY REIMAN (*J. Chim. phys.*, 1917, **15**, 293—333).—A full account of work already published (compare A., 1917, ii, 137, 200).

H. M. D.

**Revision of the Atomic Weight of Bromine. Normal Density of Hydrogen Bromide Gas.** WALLACE JENNINGS MURRAY (*J. Chim. phys.*, 1917, **15**, 334—359).—A full account of work previously published (A., 1917, ii, 201). H. M. D.

**Chemical Reactions in the Corona. I. Ozone Formation.** F. O. ANDEREGG (*J. Amer. Chem. Soc.*, 1917, **39**, 2581—2595).—An account is given of some preliminary observations which have been made on the formation of ozone during the passage of a current of oxygen through a tube in which corona discharge is maintained. The results suggest that a condition of equilibrium is rapidly attained. It is hoped that the study of this and other reactions in the corona discharge will throw some light on the connexion between ionisation and chemical reaction. H. M. D.

**Analytical Control of the Ammonia Oxidation Process.** G. B. TAYLOR and J. D. DAVIS (*J. Ind. Eng. Chem.*, 1917, **9**, 1106—1110).—In the catalytic oxidation of ammonia by means of atmospheric oxygen for the production of nitric acid, the following reactions take place:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \quad . \quad . \quad . \quad . \quad (2)$$

and the possibility of the second reaction being produced by means of an intermediate reaction,

$$4NH_3 + 6NO = 5N_2 + 6H_2O \quad . \quad . \quad . \quad . \quad . \quad (3)$$

was pointed out by Reinders and Cats (A., 1912, ii, 248). Evidence that this third reaction does take place under certain conditions has been obtained in the case of a badly constructed oxidiser, in which irregular cooling of the catalyst was produced locally by currents of the burned gases. Samples taken from points near the cool places contained ammonia, whereas in samples taken outside the catalyst chamber the proportion of ammonia was low. It was probable that most of this ammonia passing such points was subsequently "burned" by the hot nitric oxide. Effective working in a converter depends on maintaining conditions which promote reaction (1) and are unfavourable to reaction (2). [See further *J. Soc. Chem. Ind.*, 1918, **37**, 54A.]

C. A. M.

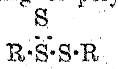
**The Solubility of Silica.** Victor Lenher and Henry Baldwin Merrill (*J. Amer. Chem. Soc.*, 1917, **39**, 2630—2638).—The solubility of silica in water and in aqueous solutions of hydrochloric and sulphuric acids of varying concentration has been measured at 25° and 90°. With gelatinous silica, a condition of equilibrium is reached after a few hours or days, but with ignited silica much longer periods are required for the attainment of saturation. The results seem to show that the solubility of gelatinous silica is independent of the method of preparation of the substance, and that ignited silica will give solutions of the same concentration when the equilibrium condition is reached.

The solubility increases with the temperature, and at a given temperature decreases with increase in the concentration of the acid. Carbon dioxide has no measurable influence on the solubility of silica. The results are not only of interest in connexion with the estimation of silica, but possess considerable geological significance. H. M. D.

**Polysulphides of the Alkali Metals. III. Solidifying Points of the Systems, Sodium Monosulphide-Sulphur, and Potassium Monosulphide-Sulphur.** John Smeath Thomas and Alexander Rule (T., 1917, **111**, 1063—1085. Compare T., 1914, **105**, 177, 2819).—The freezing-point curves for mixtures of sulphur with sodium monosulphide and potassium monosulphide, derived from observations on the rate of cooling of the mixtures in a current of dry nitrogen, show the existence of a complete series of compounds of the formula $R_2S_x$, where $x$ is a whole number having the maximum value 5 in the sodium series and 6 in the potassium series.

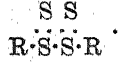
The members of the potassium series of compounds resemble closely the corresponding rubidium and cæsium compounds (Biltz and Wilke-Dörfurt, A., 1905, ii, 162; 1906, ii, 283, 611), but the sodium compounds differ from their analogues in appearance and properties. This difference is also shown in the comparative stabilities of compounds of corresponding composition and in the maximum combining power of the metals.

The rate at which the polysulphides lose sulphur when heated in a steady stream of hydrogen at regularly increasing temperatures has also been examined. The results obtained indicate that the disulphides of both metals are very stable compounds from which sulphur can only be removed with difficulty at 700—800°. This suggests that the polysulphide molecules contain two atoms of sulphur which are combined differently from the remaining atoms of sulphur. The disulphides are represented by the formula R·S·S·R, and the higher polysulphides by formulæ, such as



$$R\cdot\overset{S}{\overset{\cdot\cdot}{S\cdot S}}\cdot R$$

and



$$R\cdot\overset{S\ S}{\overset{\cdot\cdot\cdot\cdot}{S\cdot S}}\cdot R$$

Molecular weight determinations by the boiling-point method in ethyl alcohol solution gave numbers less than those required by the formula $R_2S_x$. These results favour the simple formula $R_2S_x$, as opposed to the doubled formula $R_4S_x$ suggested by Bloxam (T., 1900, **77**, 753). The difference between the actual results and those required by the formula $R_2S_x$ are attributed to ionisation.

No evidence of intermediate compounds, such as the enneasulphides (Bloxam, *loc. cit.*), has been obtained in either series.

H. M. D.

**Ammoniacal Copper-Mercury Derivatives.** F. ANDERLINI (*Gazzetta*, 1917, **47**, ii, 171—176. Compare A., 1912, ii, 764).—The *compound*, $CuHgBr_4,4NH_3$, is obtained in dark blue crystals by mixing boiling solutions of ammoniacal cupric bromide and mercury bromide dissolved in potassium bromide. If this compound is dissolved in a warm solution of ammonium bromide and the solution treated with mercury bromide dissolved in potassium bromide, free ammonia being present, but not in excess, the *compound*, $CuHg_2Br_6,4NH_3$, is obtained in bright blue scales or needles.

R. V. S.

**Observations on the Rare Earths. IV. The Purification of Gadolinium.** LOUIS JORDAN and B. SMITH HOPKINS (*J. Amer. Chem. Soc.*, 1917, **39**, 2614—2623).—The results of experiments are described in which the attempt has been made to separate gadolinium from rare earth mixtures by the fractional precipitation of the dimethyl phosphates, bromates, and glycollates.

Fractionation of the dimethyl phosphates rapidly removes europium and samarium completely, and gadolinium of considerable purity is obtained from the middle fractions. The terbium which is present in this material can be removed by fractionation of the bromates. The glycollate method rapidly removes samarium from gadolinium, but has little effect on the removal of terbium.

The method recommended for the separation of gadolinium from rare earth mixtures is first to remove cerium by the bromate method and fractionally crystallise the residue. The less soluble fractions contain only europium, samarium, gadolinium, and neodymium, which are converted into the dimethyl phosphates and again fractionated. The least soluble fractions will then consist of high-grade gadolinium. Any remaining traces of samarium can be removed by precipitation with sodium glycollate. H. M. D.

**Revision of the Atomic Weight of Samarium. Analysis of Samarium Chloride.** O. J. STEWART and C. JAMES (*J. Amer. Chem. Soc.*, 1917, **39**, 2605—2614).—A fractionation method for the extraction of samarium from its admixtures with the other rare earth metals is described. The pure samarium oxide was converted into the chloride, $SaCl_3,6H_2O$, which was dried, finely powdered, and heated below 100° until most of the water of crystallisation had been driven off. The temperature was then raised to 180°, and finally to 300°, the tube being traversed by a current of dry hydrogen chloride. The anhydrous salt was then removed, finely powdered, and heated to its melting point in contact with hydrogen chloride, which was then displaced by nitrogen and finally by air. The atomic weight of the samarium was derived from the ratio $SaCl_3:3Ag$. A series of preliminary experiments in which the individual results were not in good agreement gave a mean value Sa = 150·45, and a final series of eight determinations in close agreement gave a mean value Sa = 150·43. H. M. D.

**Precipitation, Stability, and Constitution of Hydrated Ferric Oxide Sols. I.** MARKS NEIDLE (*J. Amer. Chem. Soc.*, 1917, **39**, 2334—2350).—A systematic study of the precipitation of hydrated ferric oxide sols of varying purity and concentration by means of potassium sulphate. The sols were prepared by oxidising a solution of ferrous chloride containing 1 gram equivalent of ferrous chloride in 400 c.c. of solution by means of 3% hydrogen peroxide. The solutions were then dialysed and diluted to the required concentrations. The content of iron and chlorine was estimated, and the relative stability determined by measuring the volume of a standard solution ($M/800$ or $M/1600$) of potassium sulphate required to effect complete precipitation of the sol. A number of series of such clear sols were prepared, and in each series the iron content was constant, whilst the chlorine content varied. The results show that for a given iron concentration the stability increases with the chlorine concentration, whilst for sols of given purity, that is, for sols which have the same ratio, Fe/Cl, the stability decreases as the concentration increases, this being most pronounced in very pure sols. It is shown that the maximum purity of a sol may be ascertained by graphic extrapolation. A general discussion is given of the results of Nicolardot and Duclaux (A., 1905, ii, 167; 1906, ii, 677). The author advances a chemical theory of the constitution of hydrated ferric oxide sols to explain the relationship between stability and composition. J. F. S.

**A New Oxychloride of Tin.** HARRY F. KELLER (*J. Amer. Chem. Soc.*, 1917, **39**, 2354—2356).—During the examination of metallic objects found in the aboriginal cemetery on Hogtown Bayou, Santa Rosa County, Florida, the author noticed a number of cavities, in a piece of tin, which were lined with small, shining crystals. The crystals were mostly in the form of thin plates, but some were acicular. On heating, the substance melts and gives off acrid fumes which form a white sublimate without a trace of moisture. Analysis of a small quantity of the material leads to a composition corresponding with the formula $SnCl_2,SnO$. [See also *J. Soc. Chem. Ind.*, 1918, **37**, 29A.] J. F. S.

**Solubility of Bismuth Oxychloride in Hydrochloric Acid and its Relation to Complex Formation.** ARTHUR A. NOYES, FRANK W. HALL, and JAMES A. BEATTIE (*J. Amer. Chem. Soc.*, 1917, **39**, 2526—2532).—The electrical conductivity of a solution of hydrochloric acid is diminished by the addition of bismuth chloride. The observed diminution can be most satisfactorily interpreted on the assumption that chlorobismuthic acid of the formula $H_2BiCl_5$ is formed.

Measurements of the solubility of bismuth oxychloride in hydrochloric acid solutions of varying concentration at 25° afford support for this hypothesis in the case of the more concentrated solutions, whilst for the less concentrated acid solutions the solubility data suggest that the predominant complex acid has the formula $HBiCl_4$.

H. M. D.

## Mineralogical Chemistry.

**Crystal Structure of Copper Pyrites determined by X-Rays.** Charles L. Burdick and James H. Ellis (*J. Amer. Chem. Soc.*, 1917, **39**, 2518—2525).—The *X*-ray interference effects obtained with a crystal of copper pyrites ($CuFeS_2$) show that the iron and copper atoms together form a face-centred tetragonal lattice, the planes perpendicular to the tetragonal axis consisting of alternate layers of copper atoms and iron atoms. The sulphur atoms are located on an exactly similar face-centred lattice, the planes of sulphur atoms being situated at equal distances from the planes of iron and of copper atoms in each of the three axial directions.

The density of copper pyrites, calculated from the weights of the atoms and the distances between the atom planes, is 4·24, whilst the observed densities recorded in the literature lie between 4·1 and 4·3.

H. M. D.

**Tungstenite, a New Mineral.** R. C. Wells and B. S. Butler (*J. Washington Acad. Sci.*, 1917, **7**, 596—599).—This mineral, a tungsten sulphide, probably $WS_2$, occurs intimately intermixed with other minerals in a compact ore from the Emma mine in the Little Cottonwood district, Salt Lake Co., Utah. Under the microscope, it is seen as feathery flakes resembling graphite in appearance. It is lead-grey and opaque with metallic lustre, and soft enough to mark paper. D about 7·4 (calculated from 6·43 of the specimen analysed, allowing for impurities). The mineral is unattacked by hydrochloric or nitric acid, but is decomposed by aqua regia. It is not oxidised by roasting in air. A bulk analysis of the ore gave:

| W. | S. | Fe. | Zn. | Mn. | Ni. | Pb. | As. | Sb. | Cu. | Ag. | $SiO_2$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 44·7 | 29·1 | 8·8 | 0·4 | 0·6 | 0·3 | 4·1 | 1·0 | 0·8 | 1·3 | 0·4 | 0·3 | 0·7 | 92·5 |

corresponding with $WS_2$, 61·5; pyrites, 17·3; tennantite and tetrahedrite, 8·1; galena, 4·7%. In chemical composition and physical characters the mineral is analogous to molybdenite ($MoS_2$).

L. J. S.

**The Photographic Spectra of Meteorites.** Sir William Crookes (*Phil. Trans.*, 1917, [*A*], **217**, 411—430).—See this vol., ii, 25.

# Analytical Chemistry.

**Gas Interferometer Calibration.** JUNIUS DAVID EDWARDS (*J. Amer. Chem. Soc.*, 1917, **39**, 2382—2385).—A simple method of calibrating a Rayleigh-Zeiss gas interferometer is described. This differs mainly from the older method of using two gases of different refractive indices in using dry air free from carbon dioxide in both sides of the apparatus and changing the pressure of one side.
J. F. S.

**The Direct Determination of the Hygroscopic Coefficient.** FREDERICK J. ALWAY, MILLARD A. KLINE, and GUY R. McDOLE (*J. Agric. Research*, 1917, **11**, 147—165).—An investigation of Hilgard's method for the determination of the hygroscopic coefficient of soils (compare U.S. Dept. Agric. Div., *Chem. Bull.*, 1893, **38**). If carried out exactly as described, it gives trustworthy results, but it is more convenient to replace the sheets of glazed paper by shallow aluminium or copper trays. The absorption boxes must not be increased in size, and a larger number of samples must not be exposed in one box. The hygroscopic coefficient increases with rise in temperature (compare Lipman and Sharp, A., 1912, ii, 84). Preliminary drying of soils at 100—110° does not affect their hygroscopicity, and soils may be ground in steel mortars to pass through a 1 mm. sieve without affecting this coefficient. It is preferable to expose the soil for twenty-four rather than for twelve hours, and it is essential to use only a very shallow layer of soil. Transference of the exposed soil from the boxes to weighing bottles must be performed rapidly, or the results obtained will be too low. W. G.

**Estimation of Sulphur in Urine.** H. J. HAMBURGER (*Zeitsch. physiol. Chem.*, 1917, **100**, 221—240. Compare A., 1916, ii, 641). —Application of the method previously described to the estimation of inorganic and ethereal sulphate and of neutral sulphur in urine.
H. W. B.

**Gravimetric Estimation of Sulphuric Acid and Barium as Barium Sulphate.** Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1917, **56**, 417—439. Compare *J. Soc. Chem. Ind.*, 1918, **37**, Feb.). —An investigation of the influence of various substances on the precipitation of barium sulphate. Low results are obtained when a large excess of barium chloride is added, but when hydrochloric acid or nitric acid is also present, the results are too high. Potassium salts cause the results to be low unless hydrochloric acid is also present, when they become too high; hydrochloric acid, however, increases the low results obtained in the presence of both potassium chloride and potassium sulphate. Sodium, ammonium, zinc, magnesium, and aluminium chlorides have no effect on the precipitation, ferric chloride makes the figures for the barium sulphate to be about 3% too low, and chromium chloride has a similar effect. W. P. S.

**Estimation of Nitrogen in Explosives of the Type of Nitric Esters.** BERNARDO ODDO (*Gazzetta*, 1917, **47**, ii, 145—158).—In the method of estimation here described, the reaction between nitrates, sulphuric acid, and mercury is employed, but the process is made gravimetric instead of volumetric. The explosive is dissolved in sulphuric acid in a small conical flask in which a small test-tube containing the mercury is placed. The flask is closed with a rubber stopper which carries an inlet tube and (as an outlet) a U-tube containing sulphuric acid. Purified carbon dioxide is passed through until all air is displaced (about forty minutes). The apparatus is then disconnected from the gas supply, closed at each end with a short rubber tube and glass rod, and weighed. The end of the U-tube is then opened, the mercury is poured into the flask by inclining the latter, and the whole is shaken for a few minutes. When the reaction is complete, carbon dioxide is passed as before. After reweighing, the percentage of nitrogen can be calculated from the loss in weight. The results are satisfactory. R. V. S.

**Estimation of Metallic Iron in Ferrum Reductum.** AUGUST EBERHARD (*Arch. Pharm.*, 1917, **255**, 357—381).—Ferrum reductum used to be prepared by means of pure hydrogen at a not too high temperature, genuine ferrum hydrogenio reductum being thereby obtained. In recent years, however, impure hydrogen (containing carbon monoxide) and higher temperatures have been employed, and these changes have so altered the quality and purity of the product that the old methods of estimating the iron, particularly the iodometric methods, no longer yield trustworthy results.

For the technical method recommended, see *J. Soc. Chem. Ind.*, 1918, **37**, 39A. C. S.

**Iso- and Heteropoly-acids. XV. Analytic and Synthetic Methods for the Investigation of Heteropoly-acids.** ARTHUR ROSENHEIM and JOHANNES JAENICKE (*Zeitsch. anorg. Chem.*, 1917, **101**, 215—224).—A critical summary is given, with numerous references, of the analytical methods employed for these acids, including estimations of water, boric acid, silica, phosphoric, arsenic, molybdic, and tungstic acids and alkalis. A short outline of the general methods for preparing heteropoly-acids and salts is also given. E. H. R.

# General and Physical Chemistry.

**Refractivity of Unsaturated Compounds. I.** GERVAISE LE BAS (*Trans. Faraday Soc.*, 1917, **13**, 53—60).—A discussion of the influence on refractive power of the ethylene and acetylene linkings, of the carbonyl group, and of conjugated carbonyl groups, and of the refractivities of nitrites, nitrates, and oximino-compounds. H. M. D.

**The Line Spectrum of Titanium and its Applications.** A. DE GRAMONT (*Compt. rend.*, 1918, **166**, 94—99).—A study of the line spectrum of titanium, when fused in the form of its oxide with lithium, sodium, or potassium carbonate and submitted to the action of a condensed spark, or with the direct spark between two fragments of steel containing titanium. The spectrophotographs are reproduced in the original, together with tables showing the rays more sensitive to the eye than to a photographic plate, and those capable of being photographed. The author suggests that the approximate amount of titanium in a steel may be determined by observing which of the titanium rays can be detected. In a similar manner, this method may be used for the examination of minerals. W. G.

**The Application of the Quantum Hypothesis to Photochemistry.** E. WARBURG (*Naturwiss.*, 1917, **5**, 489—494; from *Chem. Zentr.*, 1917, ii, 587—588).—Restricting the term photochemistry to such reactions as do not yield electric end-products, it is probable that the photochemical process does not involve the separation of electrons, because gases undergoing a photochemical change do not exhibit conductivity. It is necessary to distinguish between chemical processes produced directly by the influence of light and secondary reactions. Only those rays which are absorbed exert photochemical action, and the effect is proportional to the absorbed radiation; the chemical change caused by an absorption of radiation equivalent to one gram-calorie is termed the "specific photochemical effect." The hypothesis that photochemical absorption occurs by quanta explains the concentration of the effect on relatively few molecules and accounts for the greater activity of the shorter wave-lengths, the effect being due to an increase in temperature of individual molecules. From the quantum hypothesis, it follows that a molecule, for example, of hydrogen bromide, can be directly decomposed by radiation only if $2c/\lambda > q$, where $c$ is a constant, $\lambda$ the wave-length, and $q$ the heat effect in gram-calories per molecular weight on recombination of the decomposition products. The apparent contradiction that photolysis can occur with ammonia for wave-lengths of $\lambda = 0{\cdot}209$, in which case $2c/\lambda < q$, is explained by the possibility that a molecule of ammonia after absorption of a quantum without chemical alteration may subsequently meet a second molecule, with the result that the change $2NH_3 = N_2 + 3H_2$ occurs, for which $q$ possesses a smaller value than for the decomposition of a single molecule into its constituent atoms. Processes in which the production of a false equilibrium is accompanied by a decrease and an increase of the free energy of the system are described respectively as photochemical actions of the first and second class. The photochemical yield is the proportion of the absorbed radiation which undergoes conversion into chemical energy, and in the case of the decomposition of ammonia by the wave-length 0·209 amounts to 2%, a notable parallelism appearing to exist between the yields and those of the silent discharge. If the quantum is greater than the heat change in the primary photochemical process, the excess will be converted into heat, and heat will also be produced in the secondary processes. If in a photolytic process the highest possible photochemical yield is desired and a minimum heat effect, it is necessary that the quantum should be greater than the heat change involved in the primary process, but only greater to the extent required for the fission of the photolyte, and the heat effect in the secondary processes should be as small as possible. D. F. T.

**True Photochemical Processes.** FRITZ WEIGERT (*Zeitsch. Elektrochem.*, 1917, **23**, 357—368).—A theoretical paper in which, after differentiating between ideal and real photochemical processes, and surveying a number of real photochemical reactions, the author propounds a theory of the mechanism of these processes. It is shown that a transformation of light energy into other forms of energy only occurs when the electrons rotating round the positive nucleus travel in a distorted path and when the distortion is produced by neighbouring particles which are in irregular relative motion. There must be, therefore, an optical coupling, in the sense of Stark's intermolecular influence, which is closely connected with the broadening of spectrum lines. According to the Le Chatelier-van't Hoff principle, it is to be expected that a change in the system will be brought about by the absorption of light, in the sense that the distortion will be as far as possible removed. This would occur most easily by the separation of the distorting particles from one another. The foregoing is in accord with Bohr's work (A., 1913, ii, 689, 943, 1045), and is sufficient to include all known real photochemical phenomena and the transformation of light into heat. The "equivalent law" of Einstein holds for ideal photochemical reactions, and in its deduction simple processes, without the mutual influences of neighbouring particles, alone were considered. This law may be extended by the assumption that in real photochemical processes not a single molecule, but the whole of the optically coupled particles, take part in the absorption of an energy quantum, and that therefore changes must take place over the whole of this region. This region contains fewer particles the higher the frequency of the absorbed light and the more dilute the partition of the mass; the lower the temperature, the more nearly the relationships approach those of an ideal process. The more particles displaced by the absorption of an energy quantum, the larger is the fraction of the thermal energy lost. Hence in solid and stabilised systems, changes, brought about by the absorption of energy, persist for long periods and are the cause of characteristic changes and after-effects. Changes brought about in other bands by the distortion indicate the cause of a number of characteristic colour changes effected by light. This theory differs from previous theories, inasmuch as it does not presuppose either a primary electron emission or an electron loosening. The consideration of the fact that a relative displacement of small masses brings about a distortion of the electron orbit leads at once to the meaning of luminescence phenomena. Should the displacement be the result of light absorption, then fluorescence follows. In connexion with the foregoing, the author briefly considers the photoelectric effect and the action of Röntgen rays. It is shown, in the first place, that a connexion between photochemical fluorescence and photoelectric effects does not of necessity exist, but they can in individual cases appear simultaneously. The only direct process necessarily connected with the absorption of light is the relative displacement of the individual optically coupled particles, and therewith a change in the absorption under consideration, which shows itself most clearly by its dependence on the intensity of the incident rays. J. F. S.

**The Disintegration Constant of Radiothorium.** B. Walter (*Physikal. Zeitsch.*, 1917, **18**, 584—585).—Measurements on the decay of the radiation, through 5 mm. of lead, of two preparations of radiothorium, extending over 500 days, have given a mean value for the half-period of 1·876 years, or 685 days, or 989 days for the period of average life. This is less than the accepted half-period, 2 years, and is in agreement with the recent statement of Meyer and Paneth (*Wien. Ber.*, 1916, Abt. II.*a*, **125**, 1253) that the value could not be greater than 1·9 years as a maximum. F. S.

**"Spark-lengths" in Hydrocarbon Gases and Vapours.** Robert Wright (T., 1918, **113**, 79—80. Compare A., 1917, ii, 403).—Comparative measurements of the spark-lengths have been made in hydrogen, benzene, toluene, and paraffin hydrocarbons. In the paraffin series, the spark-length decreases with increase in the molecular weight of the hydrocarbon. The insulating power of *iso*pentane is exceptionally high, being greater than that of *n*-pentane and greater also than that of hexane. The results for benzene and toluene show that the insulating power of these is approximately the same as that of hexane. H. M. D.

**The Charge and Dimensions of Ions and Dispersoids.** G. von Hevesy (*Kolloid Zeitsch.*, 1917, **21**, 129—136. Compare A., 1916, ii, 594).—Evidence is put forward in support of the view that there is a tendency for electrically charged particles to combine with water molecules until the potential of the particle is reduced to about 70 millivolts. Since the potential of a charged ion is given by $V=\epsilon/KR$, where $\epsilon$ is the charge, $R$ the radius of the particle, and $K$ the dielectric constant of the solvent medium, it follows that $R=2\cdot8\times10^{-8}$ cm. for a normal univalent ion. For a multivalent ion, the radius will be proportional to the charge.

Since the rate of diffusion of an ion depends mainly on the radius, the diffusion constants may be expected to depend on the valency. The available data for uni-, bi-, ter-, and quadri-valent ions give average values for the reciprocals of the diffusion constants, which are in the ratio 1 : 1·99 : 3·03 : 3·88. This relation is considered to afford strong support for the theory of constant ionic potential.

The combination which takes place when multivalent electrolytes are dissolved in water is supposed to be directly connected with the formation of aqueous envelopes in accordance with the above tendency. This combination is relatively small in the case of univalent electrolytes.

The ionic mobility of a normal univalent ion, for which $\epsilon=4\cdot7\times10^{-10}$, $R=2\cdot8\times10^{-8}$ cm., and $V=0\cdot07$ volt, is 48 when expressed in terms of the ordinary units. In the case of ions of large size, such as complex organic ions, there is no tendency to combine with water, in that the potential of the anhydrous ion is already less than that which tends to be set up by the interaction. In a certain sense, these slowly moving ions are to be regarded as abnormal.

The same tendency is supposed to operate in the case of colloidal particles. On the assumption that these particles are characterised by an electrical double layer at the surface of contact with the dispersive medium, the potential of the particles may be calculated from the equation $V=\epsilon(R_2-R_1)/KR_1R_2$, in which $R_1$ is the radius of the colloidal particle and $R_2-R_1$ the thickness of the electrical double layer. This thickness has been found to be about $5\times10^{-7}$ cm.

Since the mobility of the colloidal particles is of the same order as the normal ionic mobility, it is possible to utilise the above relation to obtain the connexion between the charge on a colloidal particle and its radius. It is thus found that the charge is approximately proportional to the radius in the case of very small particles, but that the charge increases much more rapidly than the radius.

In concentrated solutions of electrolytes, the ions are not entirely independent, and by taking into account the electrical interaction, it is inferred that the mobility of ions in aqueous solutions will increase with the concentration of the ions provided that a suitable correction is introduced for the change in viscosity.

In the case of fused salts, the mutual interaction becomes much more pronounced, and at the same time the proportion of neutral molecules with which the ions may combine is greatly reduced, with the result that the normal potential cannot be set up. The electrical properties of fused electrolytes, and in particular the high electrical conductivity, are to be explained in terms of these peculiarities, which distinguish the fused salts from ordinary solutions of electrolytes. H. M. D.

**The Conductivity of Dispersoids.** G. VON HEVESY (*Kolloid Zeitsch.*, 1917, **21**, 136—138. Compare preceding abstract).—If the number, size, and mobility of the particles of a colloid are known, it is possible to calculate the charge on the particles and also the conductivity of the colloidal solution.

By calculating the conductivity of a 0·1% solution of colloidal gold on various assumptions relative to the radius of the particles and comparing the results with the observed conductivity, it is possible to derive information with respect to the actual size of the particles and the charge which they carry. It is probable that the maximum conducting power of a solution of a colloidal metal is less than $0·5 \times 10^{-5}$ mho, and the size of the particles which correspond with this is represented by $R = 10^{-7}$ cm., where $R$ is the radius.

Although other colloidal substances appear to conduct somewhat better than the colloidal metals, the conductivity would appear to be in all cases less than that of a $0·0001N$-salt solution. The small conducting power of the colloids is to be attributed entirely to the small number of the particles, for the charge carried by the particles is always greater than the charge of an ion of the same size. The ratio of the charges is, in fact, given by $(R/d + 1)$, where $R$ is the radius of the particle and $d$ the thickness of the electrical double layer $= 5 \times 10^{-7}$ cm. H. M. D.

**Fallacy of Determining the Electric Charge of Colloids by Capillarity.** A. W. THOMAS and I. D. GARARD (*J. Amer. Chem. Soc.*, 1918, **40**, 101—106).—It has been suggested that positive and negative colloids can be distinguished by the difference in the capillary effects which are observed when strips of filter paper are dipped into the colloidal solutions. If the particles are negatively charged, they are said to ascend the strip readily, whereas positively charged particles are coagulated and deposited on the filter paper within a short distance of the surface of the solution.

Experiments made with colloidal solutions of ferric hydroxide, chromium hydroxide, arsenious sulphide, antimony sulphide, and molybdenum lead to the conclusion that the basis of the above method is illusory, and that there is no relation between the sign of the electrical charge and the capillary behaviour. The ascent of the colloidal particles depends on the dilution of the sol, on the presence of electrolytes, on the nature of the surrounding atmosphere, and on the nature and previous treatment of the filter-paper strip. It is probable that the supposed dependence of the capillary behaviour on the charge of the particles owes its origin to the circumstance that the observations were made with relatively concentrated solutions of the positive colloids, the negative colloidal solutions being relatively dilute. H. M. D.

**Electrochemical Behaviour of Nickel.** A. SMITS and C. A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 394—403).—Certain anomalies exhibited by nickel in its electrochemical behaviour are attributable to the slow rate at which internal equilibrium is established. In contact with air or hydrogen, the anomalous behaviour is intensified, and this appears to be due to the circumstance that oxygen and hydrogen exert a negative catalytic influence. This influence of hydrogen explains the fact that the potential of a nickel electrode in contact with an atmosphere of hydrogen is the same as that of the hydrogen electrode. In reference to the normal calomel electrode, this potential is $-0·640$ volt, whereas the true equilibrium potential measured in a vacuum is $-0·480$ volt. To obtain this value, the hydrogen-ion concentration should not exceed $10^{-3}$ gram ion per litre.
H. M. D.

**A Lead Standard Cell and a Determination of the Potential of the Lead Electrode.** W. E. HENDERSON and GEBHARD STEGEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 84—89).—It has been found that lead amalgams containing 2·5 to 6% of lead may be used for the attainment of constant and reproducible potential differences. The cell Pb amalgam$|PbSO_4|Na_2SO_4,10H_2O|Hg_2SO_4|Hg$ has an *E.M.F.* which may be represented by the equation $E_t = 0·96463 + 0·000174(t-25) + 0·00000038(t-25)^2$ for temperatures between 18° and 30°. The *E.M.F.* is reproducible to within three-hundredths of a millivolt, but a gradual diminution of the *E.M.F.* occurs when the cell is kept for an extended period of time.

From the temperature coefficient of the cell, the heat of the reaction, $0·5Pb_2Hg + Hg_2SO_4 = PbSO_4 + 2·5Hg$, is found to be 42139 cal. The value derived from thermochemical data is 41785 cal.

Measurements of the *E.M.F.* of a cell of the above type with the amalgam replaced by pure lead gave 0·96973 at 25°. The difference of 0·0051 volt is used in the derivation of the *E.M.F.* of the cell $Pb|PbCl_2|0·1NKCl|Hg_2Cl_2|Hg$, giving 0·5187 volt at 25°. This is further employed in the calculation of the potential of the normal lead electrode, using available data for the solubility and degree of ionisation of lead chloride. The *E.M.F.* of the cell obtained by combination of the normal lead electrode with the 0·1*N*-calomel electrode at 25° is 0·4696 volt. [See *J. Soc. Chem. Ind.*, 1918, March.] H. M. D.

**Effect of Interionic Forces on Electrolytes.** S. R. MILNER (*Phil. Mag.*, 1918, [vi], **35**, 214—220).—The author contends that the true degree of ionisation of an electrolyte cannot be obtained from either osmotic or conductivity data. The failure of the law of mass action in its application to solutions of strong electrolytes is said to be such that insuperable difficulties stand in the way of any theory which ascribes the variations in conductivity to changes in the number of the ions. These difficulties are avoided if the variations in conductivity are attributed to the action of the electrical field on the ionic mobility. H. M. D.

**Equivalent Conductance of Electrolytes in Dilute Aqueous Solution. I. The Water Correction.** EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1918, **40**, 106—122).—The introduction of improvements in the Kohlrausch method for the determination of the conductivity of electrolytes (compare A., 1917, ii, 10) has made it possible to obtain increased accuracy in the experimental measurement, and to investigate, in particular, the conductance of electrolytes in very dilute solution. In this paper, which forms the first of a series in which the results of these investigations are described, the author discusses the question of the magnitude and nature of the water correction, the influence of carbonic acid, and the products to which this gives rise by metathesis in dilute solutions of various kinds of electrolytes. The fact that the strong acids in very dilute solution appear to be abnormal in their conducting power, even when the observed conductivity has been corrected for carbonic acid, suggests strongly that basic or saline impurities are present, and since these affect the magnitude of the carbonic acid correction, it is considered that accurate data for the conductivity of dilute solutions can only be obtained by the use of ultra-pure water instead of water which is in equilibrium with the atmosphere. H. M. D.

**Equivalent Conductance of Electrolytes in Dilute Aqueous Solution. II. The Extrapolation of Conductivity Data to Zero Concentration.** EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1918, **40**, 122—131).—The methods previously employed by Kohlrausch, Noyes, Kraus and Bray, and by Bates for the estimation of the limiting molecular conductivity are critically examined and rejected as untrustworthy on the ground that most of these involve the assumption that the functional relation between the conductivity and the concentration, which holds for the lowest measurable range of concentrations, will also hold down to zero concentration.

A new graphical method of extrapolation is described, by which the author claims to avoid the errors involved in the "arbitrary function" methods and also those which attach to direct graphical extrapolation. The proposed method rests on two assumptions, the first of which is that with decreasing concentration ($c$), the value of $c\alpha^2/(1-\alpha)=k$ decreases and approximates to a constant value $k_0$ at extreme dilutions. According to the second assumption, the relation between $c$ and $k$ must be such that deviations from the law of mass action do not increase with the dilution. The actual procedure in applying the method consists in plotting values of $k$ against values of $c$ for different assumed values of $\Lambda_0$, and rejecting those values which cause the curve to exhibit radical changes in direction in the region of very dilute solution. It is said to be possible to determine $\Lambda_0$ with a precision of 0·01% if the conductivity data are of this order of accuracy and extend to $c=0·00002$.

The method of extrapolation described by Bates (A., 1913, ii, 466) involves the assumption of the validity of the Storch equation, but otherwise resembles the method now proposed, and when applied to the data for potassium chloride gives very nearly the same result. H. M. D.

**Equivalent Conductance of Electrolytes in Dilute Aqueous Solution. III. A Study of Dilute Solutions of Potassium Chloride.** HENRY J. WEILAND (*J. Amer. Chem. Soc.*, 1918, **40**, 131—150).—A method for the preparation of "ultra-pure conductivity water" is described in which ordinary conductivity water ($k = 0·6$ to $0·8 \times 10^6$ mho) is heated to near its boiling point in a large quartz still, a current of carefully purified air being passed through the water. The water vapour is condensed in a block-tin tube and collected in a quartz receiver. The specific conductance of the water obtained in this way may vary from 0·05 to $0·07 \times 10^{-6}$ mho at 18°, and has been used in the investigation of the conductivity of very dilute solutions of potassium chloride.

The conductivity cell, of about 3 litres capacity, is made of quartz, and is provided with co-axial cylindrical platinum electrodes, which are so constructed that the water does not come into contact with anything but platinum or quartz. The dilute solutions examined were prepared in the cell out of contact with the atmosphere by the successive introduction of small crystals of potassium chloride weighing about 0·005 gram.

The error resulting from the adsorption of salt from these dilute solutions by the quartz surface of the cell has been examined and found to be negligible.

The experimental data for solutions varying in concentration from about $0·00001N$ to $0·001N$ show that the quantity $k = c\alpha^2/1 - \alpha$ has a constant value for solutions for which the concentration is less than $0·0001N$. The results afford, therefore, direct experimental proof of the validity of the mass law in its application to the ionisation of potassium chloride at very low concentrations. The limiting value of the equivalent conductance at 18° was found to be 129·64 ± 0·02 (compare preceding abstract).

The empirical relations suggested by Bates and by Kraus for use in extrapolating to zero concentration have been tested by reference to the data for solutions between $c = 0$ and $c = 0·005$, and the conclusion is drawn that these do not reproduce satisfactorily the experimental results over this range of concentrations.

H. M. D.

**Equivalent Conductance of Electrolytes in Dilute Aqueous Solution. IV. Two Laws Governing the Ionisation Equilibrium of Strong Electrolytes in Dilute Solutions, and a New Rule by means of which the Equivalent Conductance at Infinite Dilution can be Determined from a Single Conductance Measurement.** EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1918, **40**, 150—158).—The behaviour of electrolytes in very dilute solution, as exemplified by the data for potassium chloride in the preceding paper and by the most accurate conductivity work of Kohlrausch and his collaborators, has led the author to the following general conclusions. In sufficiently dilute solutions ($c < 0{\cdot}0001N$), all uni-univalent salts of strong acids and bases are ionised in accordance with the requirements of the law of mass action, and the ionisation constant is the same for all. The values of $k = c\alpha^2/1-\alpha$ for such salts are identical in sufficiently dilute solution, and this identity persists up to concentrations which are higher the more closely the salts under comparison resemble each other. According to this second generalisation, the identity in the ionisation relations extends beyond the concentration up to which the salts in question satisfy the requirements of the mass law. In terms of the equation $\Lambda_c{}^2C/\Lambda_0(\Lambda_0-\Lambda_c)=K$, the statement implies that $K$ is independent of the nature of the salt, and on simplification this equation leads to the relation $\Lambda_0=\Lambda_c/\alpha$, where $\alpha$ is independent of the nature of the salt. For $C=0{\cdot}0001N$ this equation becomes $\Lambda_0=1{\cdot}00475\ \Lambda_c$.

Evidence in support of the above conclusions is furnished by the data for the salts of the alkali metals, which are examined in detail.

H. M. D.

**Electrolytic Deposition of Alloys and their Metallographic and Mechanical Investigation. VIII. Cathodic Deposits of Iron and Iron-Nickel Alloys obtained at the Ordinary Temperature under High Hydrogen Pressure.** ROBERT KREMANN and HERMANN BREYMESSER (*Monatsh.*, 1917, **38**, 359—384. Compare A., 1915, ii, 511).—In previous papers (*loc. cit.*) it has been shown that electrolytic iron deposited at ordinary pressures and temperatures is charged with hydrogen and admixed with ferric hydroxide; it is also brittle and hard. These conditions are shown to be due to the simultaneous liberation of hydrogen at the cathode. It is shown theoretically that the simultaneous liberation of hydrogen can be prevented if the electrolysis is carried out under a high hydrogen pressure. To test this deduction, *N*-solutions of ferrous sulphate have been electrolysed under a pressure of 20 atm. of hydrogen with a *C.D.* of 0·25 amp./$dm^2$ and 0·75 amp./$dm^2$. A further series of experiments was carried out with solutions to which 10 grams of citric acid per litre were added. In the first two cases, it is shown that the current efficiency is 99·33—99·46%, whereas in the last case it is only 88·57%. The deposits obtained in these cases have been compared with those obtained under 1 atm. pressure of hydrogen and in the presence of 0·15*N*-sulphuric acid. It is shown that the material obtained under the higher pressure is composed of larger crystals than that under the lower pressure. The hydrogen content of the high-pressure specimens is much less than that of the low-pressure specimens, whilst the hardness is very much reduced by the deposition under high hydrogen pressure. The specimens obtained under the present conditions are much less brittle than those obtained under other conditions, whereas the magnetic properties of the deposits are not affected by change in the conditions of deposition. Electrolytic iron produced under pressure when immersed in *N*-ferrous sulphate solution shows at once the equilibrium potential of $-0·417$ volt, whilst iron deposited under other conditions only reaches this value after some considerable time.

A further series of experiments was made under similar conditions with mixed solutions of ferrous sulphate $0·7N$ and nickel sulphate $0·3N$. In this case, the nickel–iron deposits did not show the improvement observed in the case of iron alone. A number of microphotographs of the deposits is appended to the paper. [See also *J. Soc. Chem. Ind.*, 1918, March.] J. F. S.

**Temperature Determinations by Eutectic Alloys.** CHARLES P. STEINMETZ (*J. Amer. Chem. Soc.*, 1918, **40**, 96—100).—Eutectic points of alloys furnish a more satisfactory means for the determination of temperature than the melting points of pure metals. In general, the eutectic point is not dependent to the same extent on the purity of the substance, and the alloys afford a more numerous series of fixed points on the scale.

The cooling curves of a number of alloys have been examined, and twelve of these found to give satisfactory eutectic temperatures ranging from 69·5° to 194·0°. The approximate composition of these low-melting eutectic alloys is recorded in the paper. [See *J. Soc. Chem. Ind.*, 1918, March.] H. M. D.

**Solubility of Sodium Sulphate as a means of Determining Temperatures.** THEODORE W. RICHARDS and VICTOR YNGVE (*J. Amer. Chem. Soc.*, 1918, **40**, 164—174).—The solubility of a substance with a large temperature coefficient may be used for the accurate measurement of temperatures. Between 15° and 25°, the solubility of sodium sulphate varies rapidly with the temperature, and since it may easily be obtained in a pure condition and readily gives a saturated solution, it has been examined with a view to its application in the measurement of temperature.

Measurements of the solubility were made at accurately determined temperatures in the neighbourhood of 15°, 17·5°, 20°, and 25°. The results are represented very closely by the equation $\log s = 0·659970 + 0·02963889t + 0·0000688925t^2$, in which $s$ is the solubility expressed as the number of grams of sodium sulphate per 100 grams of water.

It is claimed that the solubility method described will permit of the determination of temperatures to within 0·01°, and may be used for the standardisation of thermometers. H. M. D.

**The Transition Temperatures of Strontium Chloride and Strontium Bromide as Fixed Points in Thermometry.** THEODORE W. RICHARDS and VICTOR YNGVE (*J. Amer. Chem. Soc.*, 1918, **40**, 89—95).—The transition temperatures have been determined by methods described in previous papers (compare A., 1914, ii, 244).

The purification of strontium chloride can be effected by recrystallising above and afterwards below the transition temperature. It is found that barium can be readily removed by recrystallising below the transition temperature (61°), so as to obtain the hexahydrate. The calcium cannot be removed in this way, but recrystallisation above the transition temperature yields the dihydrate, from which the calcium is rapidly eliminated.

In a similar way, strontium nitrate may be purified by crystallising out under conditions which yield the anhydrous salt, whereby the calcium is removed. The barium may then be removed subsequently by recrystallising the hexahydrated chloride prepared from the partially purified nitrate.

The temperature at which the hexahydrate of strontium chloride is transformed into the dihydrate has been found to be 61·341° at atmospheric pressure on the hydrogen scale.

Preliminary experiments show that hexahydrated strontium bromide is similarly transformed into the dihydrate at about 88·62°. [See *J. Soc. Chem. Ind.*, 1918, 109A.] H. M. D.

**Theory of Specific Heats.** WALTHER JANKOWSKY (*Zeitsch. Elektrochem.*, 1917, **23**, 368—371).—A theoretical paper in which, on the basis of the older kinetic theory, it is shown that without making an assumption of an equal partition of energy it is possible to derive a formula for the specific heat of gases and vapours. This formula has the form $c = e_m n(1+i)/m \,.\, n \,.\, i$, in which $c$ is the true specific heat, that is, the heat at constant volume, $e_m$ the mean energy change, expressed in calories, of a molecule when the temperature is raised 1°, $i$ is the ratio of the change of molecular energy to that of the sum of the atomic energies, $i = {}^{e_m}/e_a \,.\, n$, and $n$ is the number of atoms in the molecule. This formula is tested on a large number of gases and vapours, and is found to give good agreement. The dependence of the specific heat on temperature is shown to be due to changes in the value of $i$. This is a direct contradiction of the theory of equal energy partition. This formula gives a simple theoretical basis to the Law of Dulong-Petit and Joule, and explains quantitatively the divergencies, and also shows that a strict following of the law is impossible. A further formula is deduced for the calculation of the ratio of the specific heat at constant pressure to that at constant volume. This has the forms $k = 1 + 2C/3c_v m$ and $k = 1/1 - 2C/3c_p m$, in which $C = 2{\cdot}98$, $k = c_p/c_v$, and $m$ is the molecular weight. J. F. S.

**Calculation of Gas Equilibria.** W. D. TREADWELL (*Zeitsch. Elektrochem.*, 1917, **23**, 270—272).—A mathematical paper, in which by a series of approximations the author shows that the value of $a$, the chemical constant, which is expressed by Planck as $a = R \log_e p - C'p \log_e T + r_0/T$, can on thermodynamic grounds be proved to have the value $a = R \log_e p + r_0/T - Cp \log_e T$. In both equations $p$ is the vapour pressure, $C'p$ the specific heat at constant pressure of the vapour, $r_0$ the heat of vaporisation at absolute zero, and $Cp$ the specific heat of the liquid phase. J. F. S.

**Specific Heat of Liquid Ammonia.** NATHAN S. OSBORNE and MILTON S. VAN DUSEN (*J. Amer. Chem. Soc.*, 1918, **40**, 1—13).—Measurements of the specific heat of liquid ammonia have been made according to two independent methods. In one of these, the change in temperature produced by a measured quantity of heat under saturation conditions was determined, whilst in the other the calorimeter was kept full of liquid at constant pressure greater than the saturation pressure, the change in temperature produced by the added heat energy being corrected for the heat content of the expelled liquid.

The interval of temperature covered by the measurements ranges from −45° to 45°, and over this range the specific heat increases from 1·058 at −45° to 1·173 at 45°. The dependence of the specific heat on the temperature is represented by the empirical equation $c = 0{\cdot}7498 - 0{\cdot}000136\theta + 4{\cdot}0263/\sqrt{133-\theta}$, in which $c$ is expressed in terms of the 20° calorie and $\theta$ is the temperature. H. M. D.

**Latent Heat of Vaporisation of Ammonia.** NATHAN S. OSBORNE and MILTON S. VAN DUSEN (*J. Amer. Chem. Soc.*, 1918, **40**, 14—25).—The calorimeter used in the determination of the specific heat of liquid ammonia (compare preceding abstract) was modified so as to render it suitable for the measurement of the heat of vaporisation. A known quantity of heat, developed and measured electrically, is employed to vaporise a portion of the liquid ammonia contained in the calorimeter, the ammonia vapour being withdrawn at measured temperature and pressure and its amount estimated. Corrections due to thermal leakage were reduced to a minimum by special methods of manipulation.

The results obtained show that the latent heat of vaporisation decreases from 333·0 cal. at −42° to 252·6 cal. at 49°. The variation of the latent heat with the temperature may be expressed by the empirical equation $L = 32{\cdot}968\sqrt{133-\theta} - 0{\cdot}5895(133-\theta)$, in which $\theta$ represents the actual temperature and 133 represents the critical temperature.

From the latent heat of vaporisation and the specific heat of the liquid under the pressure of its saturated vapour, the authors have calculated the specific heat of saturated ammonia vapour. Expressed in joules per gram per degree, this varies in a continuous manner from −4·42 at −45° to −3·36 at 45°. To reduce these numbers to 20° calories, they must be divided by 4·163.

H. M. D.

**The Vapour Pressure of Liquid Ammonia up to the Critical Temperature. II.** FREDERICK G. KEYES and R. B. BROWNLEE (*J. Amer. Chem. Soc.*, 1918, **40**, 25—45).—The vapour pressures of liquid ammonia have been measured between 0° and the critical temperature by a method involving the use of a piston gauge. The dependence of the vapour pressure on the temperature may be expressed by the equation $\log p = -1969{\cdot}65/T + 16{\cdot}19785 - 0{\cdot}0423858T + 5{\cdot}4131 \times 10^{-5}T^2 - 3{\cdot}2715 \times 10^{-8}T^3$. This equation holds satisfactorily for vapour pressures down to the freezing point (−77°). The boiling point was found to be −33·20 ± 0·05°. H. M. D.

**Formula giving the Saturated Vapour Pressure of a Monatomic Liquid.** E. Ariès (*Compt. rend.*, 1918, **166**, 193—197).—The author deduces the formulæ $\Pi = \tau^{\frac{5}{2}} Z / x$ and

$$x = \left(1 + \frac{(1-\tau)(0{\cdot}84-\tau)}{2\tau^2 + 1{\cdot}20}\right)\tau^{\frac{3}{4}},$$

where $\tau$ is the reduced temperature and $\Pi$ is the reduced pressure of the saturated vapour, and shows that the calculated results agree with the observed results in the cases of krypton, xenon, and argon. W. G.

**Vapour Pressures of Liquid Metals.** Joel H. Hildebrand (*J. Amer. Chem. Soc.*, 1918, **40**, 45—49).—It has been shown previously (A., 1915, ii, 416) that the heat of vaporisation divided by the absolute vaporisation temperature is the same for all normal liquids provided that comparison is made at temperatures for which the concentrations of the saturated vapours have the same value. On the basis of this relation, it is possible to superimpose the vapour-pressure curve for one substance on that of another by means of a single constant, $a$, which expresses the ratio of the absolute temperatures referred to above.

By taking mercury as the standard liquid, for which the vapour pressure may be represented by the equation $\log p = -3140/T + 7{\cdot}85$, it is shown that the vapour pressures of a number of other liquid metals may be expressed by the equation $\log p = -3140a/T + 7{\cdot}85 + \log a$, in which $a$ varies from 1·74 for cadmium to 4·90 for iron.

By means of the tabulated values of $a$ for the different metals, it is possible to calculate the vapour pressure at any temperature and also the heat of vaporisation. H. M. D.

**Apparatus for the Determination of Boiling Points.** Alfred Edwards (*J. Soc. Chem. Ind.*, 1918, **37**, 38T).—A simple form of boiling-point apparatus is described which provides for the complete immersion of the thermometer stem in the heated vapour. The still-head is traversed by a somewhat narrower inner tube with a hole near the top, through which the vapour from the boiling liquid escapes into the outer tube, passing therefrom to a condenser tube which is sealed into the still-head at its lower end. The condensed liquid tends to seal the space between the inner and outer tubes in its lower portion, and thereby to secure a regular stream of vapour through the inner tube in which the thermometer is supported. H. M. D.

**The Heat of Formation of Liquid Water from its Ions.** J. A. Muller (*Bull. Soc. chim.*, 1918, [iv], **23**, 8—13).—Using the method previously described (compare A., 1913, ii, 115), the author has determined the heats of reaction of sulphuric and hydrochloric acids with potassium hydroxide in aqueous solution at infinite dilution, and from his results has calculated the heat of formation of water from its ions. The values obtained were, with sulphuric acid 13,966 cal., and with hydrochloric acid 14,003 cal. W. G.

**Thermochemical Studies. The Heat of Combustion of the Paraffins.** DANIEL LAGERLÖF (*J. pr. Chem.*, 1917, [ii], **96**, 123—124. Compare A., 1905, ii, 76).—The heat of combustion of *n*-octane observed by direct measurement (Richards and Jesse, A., 1910, ii, 269) agrees closely with the value calculated with the aid of the author's hypothesis (*loc. cit.*), which thereby receives confirmation. D. F. T.

**The Heat of Ionisation, in Aqueous Solution, of Crystalline Barium Sulphate and the Solubility of this Salt in Water.** J. A. MULLER (*Bull. Soc. chim.*, 1918, [iv], **23**, 13—16).—From measurements of the heats of reaction of barium chloride and sulphuric acid at increasing dilutions, and determining the limits towards which these tend at three temperatures, the following expression is found for the value of $q$, the heat of combination of the ions Ba and $SO_4$, $q = 105502{\cdot}32 - 696{\cdot}857T + 1{\cdot}2118T^2$, $T$ being the absolute temperature. The heat of ionisation of crystalline barium sulphate in aqueous solution is the inverse of this. From this it is possible to calculate the ratio of the solubilities of barium sulphate at different temperatures, and the results agree with those of van't Hoff. [See also *J. Soc. Chem. Ind.*, 1918, March.] W. G.

**Adsorption Compounds and Adsorption. II. Replacement from the Surface.** L. BERCZELLER and ST. HETÉNYI (*Biochem. Zeitsch.*, 1917, **84**, 118—136).—Stalagmometric measurements of the effect of addition of alcohols to solutions of various crystalloid and colloid substances. S. B. S.

**Utilisation of the Adsorptive Power of Fuller's Earth for Chemical Separations.** ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1918, **40**, 312—328).—A comparison has been made of the adsorptive capacities of thirty-six samples of fuller's earth and other similar clays by experiments on the adsorption of quinine bisulphate and methylene-blue. The adsorptive power of a given quantity of a particular sample increases with the concentration of the unadsorbed substance in the aqueous solution and also with the time of contact, although the rate of adsorption gradually diminishes.

The method of measurement consisted in mixing 1 gram of the fuller's earth sample with 10 c.c. of water and adding to the mixture measured volumes of 1% quinine bisulphate or 0·5% methylene-blue solution. The tubes containing the mixtures were shaken for half an hour, and the solutions then examined for the adsorbed substances. From a series of such tests it was possible to obtain comparative numbers for the adsorption powers of the samples.

In the case of both the quinine salt and the methylene-blue, the free base only is adsorbed. When both are present in the solution in equal amounts, they are adsorbed to very nearly the same extent. If the fuller's earth is first shaken with methylene-blue and then with quinine bisulphate, a small amount of the latter is adsorbed and only a trace of the former liberated. If the order is reversed, a much larger proportion of methylene-blue is adsorbed and a considerable amount of the quinine salt is displaced.

The experiments show, further, the influence of dilution, of the acidity of the solution, and of the presence of ethyl alcohol and sucrose. [See also *J. Soc. Chem. Ind.*, 1918, March.]

H. M. D.

**Preparation of Uniform Collodion Membranes for Dialysis.** CHESTER J. FARMER (*J. Biol. Chem.*, 1917, **32**, 447—453. Compare Brown, A., 1917, ii, 362).—The membrane is prepared by filling a glass tube with collodion solution, inverting, and allowing to drain for one minute. The tube is then dried in a current of air for one minute and afterwards filled with cold water. After a few minutes, the thin membrane can be removed from the walls of the glass tube with the aid of a pair of forceps. Convenient apparatus for performing these operations is described in detail in the original paper.

H. W. B.

**The Colloidal Membrane: its Properties and its Function in the Osmotic System.** FRANK TINKER (*Trans. Faraday Soc.*, 1917, **37**, 133—140).—Although it is probable that the average kinetic energy of a molecule in the liquid state is the same as in the state of vapour, this must not be taken to imply that the average pressure of a solute molecule has the same value in the two states. In the solution, a large proportion of the volume is occupied by the solvent molecules, with the result that the free space is greatly reduced, and the pressure which the solute molecules would exert on an imaginary flame is consequently much greater than the corresponding gas pressure.

The internal bombardment pressure of the solute must therefore not be confused with the osmotic pressure, which, in the author's opinion, is an external mechanical pressure. The supposed analogy between osmotic and gas pressure is also considered to have no real foundation, in that this analogy fails to account for the fundamental phenomena of diffusion. The mechanism involved in an osmotic system is said to be quite different from that which produces gas pressure, there being no pressure on the membrane unless the solution is compressed. This pressure is then exerted by the solution as a whole and not by the individual molecules, whether of solute or solvent.

The similarity between a dilute solution and a gas is due to the fact that both experience no change in internal energy when the volume is varied. Equality in this respect does not, however, afford any proof that the mechanism involved in gas and osmotic pressure is of the same nature.

Reference is made to the importance of the study of the properties of the membrane, and a brief account is given of the author's work on this subject. H. M. D.

**Kinetic Theory of Osmotic Pressure.** ALFRED W. PORTER (*Trans. Faraday Soc.*, 1917, **13**, 123—132).—The cause of osmotic pressure is discussed, and it is pointed out that the kinetic theory is the only theory yet advanced which reproduces directly the values for the osmotic pressure which have been actually obtained in experiments with dilute solutions. The arguments against the kinetic theory, which rest largely on the dissimilarity of the conditions in liquids and gases, have been greatly weakened as the result of observations on the Brownian motion. These observations afford the experimental basis for a kinetic theory of liquids, according to which solute and solvent molecules are in a state of rapid movement. The osmotic pressure represents the dynamical effect of this thermal motion of the solute molecules, and in order to obtain a mental picture of the effect of the presence of the solute, it may be supposed that the molecular bombardment of the molecules of the solute on the boundary surface tends to enlarge the boundaries, and thereby to relieve the total pressure on the solvent. In other words, the kinetic pressure resulting from the thermal agitation of the solute molecules acts outwardly and diminishes the Laplacian pressure by an equivalent amount.

It is shown that the data for the osmotic pressures of sucrose solutions at 20° can be represented satisfactorily by the equation $P(v-b)=RT$, in which $b$ is a constant which is greater than the volume of the sucrose. On the assumption that this is due to the hydration of the sucrose molecules, it is found that about 5·3 molecules of water are associated with a molecule of sucrose.

If this equation is applied to the whole of Morse's results and hydration values calculated for different concentrations and temperatures, the numbers are not quite regular, but show clearly that hydration diminishes with increasing concentration. The values for dilute solutions are surprisingly high, but are considered to be quite plausible, and it is suggested that the variation in solubility with the temperature may be due to changes in the degree of hydration.

According to the equation connecting osmotic pressure with the latent heat of dilution of the solution, the latter quantity depends on the variation of $P/T$ with the temperature $T$. If these variations, derived from Morse's values at 10° and 30°, are compared with those calculated from measurements of the heat of dilution at 20°, the degree of correspondence is found to be quite satisfactory. H. M. D.

**Osmotic Pressure in Relation to the Constitution of Water and the Hydration of the Solute.** W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1917, **13**, 141—155).—The author's previous work on the properties of solutions is considered with reference to the kinetic interpretation of osmotic pressure. This interpretation rejects the idea that the molecules of the solute are directly responsible for the osmotic pressure, and a modified gas theory is put forward which involves the assumption that water is a mixture of three kinds of molecules, vapour, liquid, and ice molecules, represented by $H_2O$, $(H_2O)_2$, and $(H_2O)_3$ respectively, and attributes the osmotic pressure to the thermal agitation of the vapour molecules. The validity of the ideal gas equation for dilute solutions is supposed to indicate that these hydrol molecules comport themselves towards changes of pressure and temperature in the same way as the molecules of a gas.

The addition of a solute to water is said to be accompanied by a reduction in the proportion of both the vapour and ice molecules in the equilibrium mixture, resulting in a diminution of the vapour pressure and a lowering of the freezing point. Reduction of the molecular interspace by external pressure raises the vapour pressure, and the osmotic pressure is defined as the liquid pressure under which the external vapour pressure of a solution is equal to the internal vapour pressure of the pure solvent.

The relations between the osmotic pressure, the lowering of the vapour pressure, and the freezing point are discussed in reference to the above theory, and it is claimed that the various osmotic data are brought into line with other properties by the assumption that the active hydrol molecules enter into combination with the solute molecules. It is said that different properties lead to the same value for the degree of hydration of the solute. H. M. D.

**Solubility and Internal Pressure.** JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1918, **40**, 198).—Corrections to a previous paper (this vol., ii, 36). H. M. D.

**Changes in Volume during Solution. III.** GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1918, **40**, 192—193).—If $AB$, $A'B'$, $AB'$, and $A'B$ represent the four salts formed by the ions $A$, $B$, $A'$, and $B'$, then the apparent volume in solution of one of these may be obtained if the apparent volumes in solution of the three others are known. The calculation depends on the fact that the sum of the apparent volumes of $AB$ and $A'B'$ is equal to the sum of the apparent volumes of $AB'$ and $A'B$.

The apparent volume of dissolved calcium carbonate obtained in this way from the apparent volumes of calcium chloride, sodium carbonate, and sodium chloride is 3·0 c.c. Since the molecular volume of solid calcium carbonate is 36·9 c.c., the change in volume on dissolution is $3·0 - 36·9 = -33·9$ c.c. per mol. The contraction is thus more than 90% of the volume of the solid salt. H. M. D.

**The Structure in Steps in certain Anisotropic Liquids.** F. GRANDJEAN (*Compt. rend.*, 1918, **166**, 165—167).—This structure, already found in ethyl azoxybenzoate and cinnamate (compare *Bull. Soc. franç. Min.*, **39**, 167), has been found also in the oleates and the positive phase of cholesteryl decoate. It is described in detail. This structure in steps, and particularly the existence of steps of extremely slight thickness, separated from steps infinitely near by abrupt lateral surfaces, reveals a discontinuous property of the liquid, which is not observed in the group of azoxyphenetole.

W. G.

**Precipitation of Colloidal Gold and Platinum on Metallic Surfaces.** ELLWOOD B. SPEAR and KENNETH D. KAHN (*J. Amer. Chem. Soc.*, 1918, **40**, 181—184).—The precipitation of colloidal gold and platinum solutions when brought into contact with polished plates of zinc, steel, nickel, lead, tin, copper, or platinum has been examined, with results which indicate that the rate of coagulation increases with the electro-positive character of the metal. The effect also depends on the nature of the metal surface, in that the rate of coagulation for a given metal decreases if the surface is roughened or if the metal is employed in a finely divided condition.

It is suggested that ions of the active metal are formed, and that these are adsorbed by the colloidal particles, thereby neutralising their negative charge. In support of this view, it has been found that copper does not bring about coagulation if the colloidal gold or platinum solution is freed from air by the passage of a current of purified hydrogen. [See *J. Soc. Chem. Ind.*, 1918, March.]

H. M. D.

**Laws of Chemical Equilibrium.** ERSKINE D. WILLIAMSON and GEORGE W. MOREY (*J. Amer. Chem. Soc.*, 1918, **40**, 49—59).—A theoretical paper in which the authors derive general equations for the equilibrium in heterogeneous chemical systems by methods which are essentially based on the work of Gibbs. Special forms of equations applicable to systems of simple type are specifically referred to.

H. M. D.

**Pressure-Temperature Curves in Univariant Systems.** GEORGE W. MOREY and ERSKINE D. WILLIAMSON (*J. Amer. Chem. Soc.*, 1918, **40**, 59—84. Compare preceding abstract).—The pressure-temperature curves for univariant systems are discussed in reference to Gibbs's equations. The conditions under which different pressure-temperature curves become coincident are examined, and a method is developed by which the order of succession of the pressure-temperature curves intersecting at an invariant point can be determined. The applicability of the method is shown by reference to the five curves which melt in the quintuple points characteristic of the ternary system $H_2O$–$K_2SiO_3$–$SiO_2$.

H. M. D.

**Univariant Equilibria in the Ternary System–Water, Sodium Sulphate, Ammonium Sulphate.** C. MATIGNON and F. MEYER (*Compt. rend.*, 1917, **165**, 787—789).—The experimental data recorded show the composition of solutions which are in equilibrium with two solid substances. The two sulphates combine to form the double sulphate $NaNH_4SO_4,2H_2O$, and numbers are given for solutions saturated with respect to the double salt and Glauber's salt between −13° and 25·5°, double salt and anhydrous sodium sulphate between 29° and 58°, double salt and ammonium sulphate between −19° and 58°, and with respect to anhydrous sodium sulphate and ammonium sulphate between 62·5° and 109°.

A solution saturated with sodium sulphate boils at 102° and contains 2·10 mols. per 1000 grams of solution. Similarly, the b. p. of saturated ammonium sulphate solution is 108·9°, and it contains 3·922 mols. per 1000 grams, whilst a solution saturated with respect to the two sulphates boils at 111° and contains 1·125 mols. $Na_2SO_4$ and 3·175 mols. $(NH_4)_2SO_4$ per 1000 grams of solution. [See, further, *J. Soc. Chem. Ind.*, 1918, 29A.] H. M. D.

**Heterogeneous Equilibria between Aqueous and Metallic Solutions.** G. McP. Smith and S. A. Braley (*J. Amer. Chem. Soc.*, 1918, **40**, 197).—A correction of results recorded in a previous paper (A., 1917, ii, 455).—The error necessitates a further investigation of the ionisation relations in mixtures of sodium and strontium chlorides. H. M. D.

**Invariant Equilibria in the Ternary System: Water–Sodium Sulphate–Ammonium Sulphate.** C. Matignon and F. Meyer (*Compt. rend.*, 1918, **166**, 115—119).—A study of the equilibrium of the solution in the presence of the various combinations of three solid phases, the cooling curves being plotted. In a trilinear diagram, with co-ordinates giving respectively the temperature, the concentration of anhydrous sodium sulphate, and the concentration of ammonium sulphate, are shown the surfaces corresponding with the states of equilibrium of the solution with respect to one solid phase. [See also *J. Soc. Chem. Ind.*, 1918, March.] W. G.

**Effect of Hydrogen Chloride on the Nitrogen–Hydrogen Equilibrium.** E. B. Ludlam (*Trans. Faraday Soc.*, 1917, **13**, 43—52).—The observations made by Deville suggest that the stability of ammonia at high temperatures is increased very considerably by the presence of hydrogen chloride and lead to the supposition that the equilibrium between nitrogen, hydrogen, and ammonia will be displaced in favour of the ammonia if hydrogen chloride is added to the mixture.

Experiments in which a mixture containing equivalent quantities of nitrogen, hydrogen, and hydrogen chloride was subjected to the action of an electrically heated platinum wire or carbon rod stretched along the axis of a water-cooled tube afforded no evidence in support of the above hypothesis. The soaking of the carbon rod in solutions of sodium, calcium, or magnesium chloride made no difference to the result.

Other experiments, in which a mixture of nitrogen and hydrogen was passed slowly through a quartz tube containing sugar charcoal at about 800° gave results which seemed to show that the ammonia formed was increased when hydrogen chloride was added to the nitrogen–hydrogen mixture, although the effect was much smaller than that calculated from the mass action equation.

On the assumption that the smallness of the effect was due to the slowness of the reaction, attempts were then made to approach the equilibrium condition by starting with ammonium chloride. Weighed quantities of this were accordingly heated in an evacuated quartz tube in presence of gold, silver, copper, and iron, with results which seemed to show that ammonium chloride is not nearly so stable at high temperatures as Deville's observations would suggest.

The evidence afforded by these experiments pointed to iron as the most active catalyst, and further observations were therefore made in which nitrogen, hydrogen, and hydrogen chloride were passed through a layer of iron asbestos heated at about 450°. Even at this low temperature, ferrous chloride is formed and sublimes, and the volatility of this substance would evidently be a serious obstacle to the use of iron in practice, even if the catalytic activity of the metal were very considerable. H. M. D.

**Equilibrium Data on the Polybromides and Polyiodides of Potassium.** G. A. LINHART (*J. Amer. Chem. Soc.*, 1918, **40**, 158—163).—On the assumption that $KBr_3$ and $KBr_5$ are present in aqueous solutions which contain potassium bromide and bromine, the constitution of the solution is determined by the equations $[Br_3']/[Br'][Br_2]=K'$ and $[Br_5]/[Br_3][Br_2]=K''$. By reference to Worley's data for 26·5°, it is shown that $K'$ remains very nearly constant $=15·9$ if it is assumed that $K''=1·2$. At 0° $K'=19·6$ and $K''=2·08$, and at 32·6° $K'=15·5$ and $K''=1·06$.

From the values of the constants at the two lower temperatures, the author calculates the heat of the reactions $Br'+Br_2(aq)=Br_3'-1290$ cal. and $Br_3'+Br_2(aq)=Br_5'-3390$ cal.

When the value $K''=1·2$ for 26·5° is applied to solutions which are saturated with bromine, the calculated value of $K'$ is appreciably higher than that indicated above, and it is suggested that this may be due to the formation of $KBr_7$.

Measurements of the ratio of distribution of iodine between carbon tetrachloride and water at 25° show that the ratio of the concentrations, expressed in mols. per 1000 grams of solvent, is constant $=57·7$.

The constitution of iodine–potassium iodide solutions is also discussed briefly. H. M. D.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. X. Equilibria in Binary Solutions of *p*-Toluidine and Carbamide respectively with Nitro-derivatives of Benzene.** ROBERT KREMANN and BRUNO PETRITSCHEK (*Monatsh.*, 1917, **38**, 385—404. Compare A., 1905, ii, 307; 1906, ii, 268; 1912, ii, 1151).—The binary systems *p*-toluidine with the three dinitrobenzenes, 2:4-dinitrotoluene and the three nitrophenols respectively, and carbamide with the three dinitrobenzenes and 2:4-dinitrotoluene respectively, have been investigated by means of time-cooling curves. It is shown in the case of *p*-toluidine with the three dinitrobenzenes and with 2:4-dinitrotoluene gives no compounds, but only simple eutectics; with *m*- and *p*-nitrophenols, a compound is formed in each case. With *m*-nitrophenol and *p*-toluidine, the compound produced consists of one molecule of each constituent, whilst with *p*-nitrophenol, the compound consists of two molecules of *p*-nitrophenol to one molecule of *p*-toluidine. In the case of *o*-nitrophenol and *p*-toluidine, no compounds are formed, but simply a eutectic. Carbamide does not form any compounds in any of the mixtures examined, and in all cases there are large gaps in the mixture series. As a result of the experiments, the authors state that the tendency to compound formation with the dinitrobenzenes is determined by the residual affinity of the benzene nucleus and not by the affinity of the amino-group, whereas in the case of the nitrophenols the amino-group is the determining factor. J. F. S.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XI. Binary Solution Equilibria between Phenol and the Three Isomeric Nitrophenols respectively with the Three Isomeric Phenylene Diamines.** ROBERT KREMANN and BRUNO PETRITSCHEK (*Monatsh.*, 1917, **38**, 405—444. Compare preceding abstract).—By means of cooling curves, the authors have investigated the twelve possible binary systems formed between phenol and the three nitrophenols on the one hand and the three phenylenediamines on the other. The system phenol–*p*-phenylenediamine gives rise to the compound consisting of one molecule of diamine to two molecules of phenol. This compound forms a eutectic with phenol at 40° and with *p*-phenylenediamine at 94°. The system phenol–*m*-phenylenediamine gives rise to a compound made up of three molecules of phenol and two molecules of the diamine; this compound forms a eutectic with phenol at 24° and with diamine at 41°, and has m. p. 52·6°. In the case of the system phenol–*o*-phenylenediamine, two compounds appear; these consist respectively of four molecules of phenol and one molecule of the diamine, and one molecule of each component. The eutectics in the case of the first compound lie at 28° with phenol and 29° with the second compound. The system *p*-nitrophenol–*o*-phenylenediamine forms a single compound composed of two molecules of nitrophenol and one molecule of the diamine (m. p. 87·9°). This compound with nitrophenol has a eutectic at 85·5° and with diamine at 78°. A compound of similar composition is formed in the system *p*-nitrophenol–*m*-phenylenediamine; this melts at 119·9°, and its eutectics lie at 102° with nitrophenol and 52·4° with the diamine. In the system *p*-nitrophenol–*p*-phenylenediamine, two compounds are found; these have compositions: (*a*) four molecudes of nitrophenol to one molecule of the diamine, and (*b*) one molecule of nitrophenol to one molecule of the diamine respectively. The eutectics lie at 109·5° for *p*-nitrophenol and compound *a*, 117·5° for compound *a* and compound *b*, and 107° for the compound *b* and the diamine. The systems *o*-nitrophenol and the three phenylenediamines do not give rise to compounds; the eutectics in these cases lie at 42·5° for *p*-phenylenediamine, 33·5° for *m*-phenylenediamine, and 38·8° for *o*-phenylenediamine. The system *m*-nitrophenol–*m*-phenylenediamine gives rise to two compounds, composed of two molecules of nitrophenol and one molecule of the diamine, and one molecule of nitrophenol and one molecule of the diamine respectively. In the system *m*-nitrophenol–*o*-phenylenediamine, two compounds are found; these are two molecules of nitrophenol with one molecule of *o*-phenylenediamine and an equimolecular compound. Similar relationships are found in the system *m*-nitrophenol–*p*-phenylenediamine. J. F. S.

**A Complete Review of Solutions of Oceanic Salts. III.** ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1918, **102**, 41—65. Compare A., 1917, ii, 527).—In the previous paper, a graphic representation was devised for the doubled ternary system $(Na_2,K_2,Mg)(Cl_2,SO_4)$ in presence of sodium chloride as a constant solid phase. The diagram took the form of a triangle for any particular temperature, the corners of the triangle corresponding with the three salts $MgCl_2$, 2KCl, $Na_2SO_4$. The temperature co-ordinate being perpendicular to the plane of the triangle, the complete diagram took the form of a three-sided prism. Although sodium chloride is always present as a solid phase, the quantity in solution or the quantity of water corresponding with saturation with salt at different temperatures has been hitherto neglected. In the present paper this new factor is taken into account. At first the new variable is considered in connexion with the simple salts represented by the corners of the triangle, and later with respect to the systems associated with the sides. For an interpretation of the numerous diagrams given the original paper must be referred to. [See, further, *J. Soc. Chem. Ind.*, 1918, March.]

E. H. R.

**Chemical Kinetics.** U. PRATOLONGO (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 182—190).—The author bases on Marcelin's work (Contribution à l'étude de la cinétique physico-chimique, Thesis, Paris, 1914) the essentials of a new thermodynamics of irreversible phenomena. T. H. P.

**Effect of Temperature and of Pressure on the Limits of Inflammability of Mixtures of Methane and Air.** WALTER MASON and RICHARD VERNON WHEELER (T., 1918, **113**, 45—57).—Theoretical considerations indicate that the effect of increasing the initial temperature of mixtures of inflammable gases with air should be to widen the difference in the composition of the mixtures which correspond with the upper and lower limits of inflammability.

Experiments made with mixtures of methane and air show that the percentage of methane, corresponding with the lower limit, decreases from 6·00% of methane, when the initial temperature of the mixture is 20°, to 3·25% for an initial temperature of 700°. In the case of the higher limit mixture, the percentage of methane increases slowly with the initial temperature of the mixture up to about 600°, after which there is a considerable augmentation of the rate of increase of the methane content. It is suggested that this is probably due to the disturbing influence of surface combustion of the methane during the interval which elapses between the introduction of the gas mixture into the heated explosion vessel and the passing of the igniting spark. In general, the results obtained for the influence of the initial temperature on the limits of inflammability agree closely with those obtained by Taffanel (*Compt. rend.*, 1913, **157**, 593).

Experiments made to determine the influence of pressure on the composition of the limit mixtures show that the percentage of methane increases with pressure for both the lower and upper mixtures. This result is in agreement with previous observations made by Terres and Plenz (*J. Gasbeleucht.*, 1914, **57**, 990, 1001, 1016, 1025). The smaller effect obtained by these authors in the case of the upper limit mixtures is presumed to be due to the circumstance that they did not make use of a sufficiently powerful source of ignition in order to obtain strictly comparable results.

The lowest pressure at which self-propagation of flame occurs in mixtures of methane and air was found to be 120 mm. when the initial temperature was atmospheric. In similar experiments, Burrell and Robertson (U.S. Bureau of Mines, Technical Paper No. 121, 1916) obtained a limiting pressure of 300 mm. The difference between the two results is explicable on the asumption that the igniting source employed by these authors was not sufficiently powerful. In these circumstances, their results give merely the limiting pressure for ignition by a spark discharge of particular intensity.

The mixtures which correspond with the lowest limiting pressures contain between 8·75 and 9·40% of methane, these numbers being derived from observations in which the initial temperatures were 20°, 250°, and 500°. H. M. D.

**The Saponification of Fats. II.** J. P. Treub (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 343—357. Compare A., 1917, ii, 528).—From a mathematical discussion of the ideal case in which the saponification of a triglyceride takes place in solution, the ester groups being equivalent and no complications arising, it is shown that the relative concentration of free glycerol at any moment is equal to the third power of the relative concentration of the free fatty acid, in the case of stagewise saponification, that is, passage through the di- and mono-glycerides. The same holds good for the ideal case of esterification. The experimental results obtained when trilaurin is saponified with strong sulphuric acid show only very slight deviations from this rule, the deviations being due to the fact that the three ester groups are not perfectly equivalent. Rather greater deviations are found in the esterification of lauric acid and glycerol by strong sulphuric acid. [See also *J. Soc. Chem. Ind.*, 1918, March.] W. G.

**Dynamics of Nitrile Formation from Acid Anhydrides and Amides. I. Investigation of the Reaction $O(COPh)_2 + COPh{\cdot}NH_2 \longrightarrow 2Ph{\cdot}CO_2H + PhCN$, by Methods based on the Phase Rule.** Robert Kremann and Max Wenzing (*Monatsh.*, 1917, **38**, 445—456).—In a series of experiments designed for the investigation of the binary mixture, benzoic anhydride–benzamide, the authors found that the temperature of the primary crystallisation varied with the time during which the mixture had been heated and also with the temperature. This they were able to show was due to the reaction $O(COPh)_2 + COPh{\cdot}NH_2 \longrightarrow 2Ph{\cdot}CO_2H + PhCN$. To follow this reaction, mixtures of the four substances taking part were made in a number of different proportions, commencing with 100% of the substances on the right hand side of the equation and ending with 100% of the substances on the left hand side, but always so that the molecular ratio of the benzoic acid to the benzamide was 2:1 and that of the benzoic anhydride to the benzamide was 1:1. These mixtures were rapidly heated to 98° and then allowed to cool, and the temperature of primary crystallisation noted. The crystallisation temperatures were plotted against the composition and an analytical curve produced, which on the assumption that no chemical change had occurred gives the composition of any mixture, in which the proper ratios of the two sides of the equation are maintained, directly from the temperature of its primary crystallisation. The reaction was then studied: quantities of benzoic anhydride and benzamide in molecular proportions were mixed in a closed vessel heated to 98° or 123°, and the temperature of primary crystallisation measured at stated intervals of time (one to one hundred hours), and from the analytical curve the progress of the reaction ascertained. It is shown that the reaction is bimolecular, and at 98° has a value $k = 0{\cdot}053$, whilst at 123° $k = 0{\cdot}24$. The temperature-coefficient is therefore 1·8 for 10°. It is shown also that the reverse reaction does not take place to the extent of more than 1%. J. F. S.

**Influence of Carbon Monoxide on the Velocity of Catalytic Hydrogenation.** Edward Bradford Maxted (*Trans. Faraday Soc.*, 1917, **13**, 36—42).—Measurements have been made of the rate of absorption of hydrogen by olive oil at 180° in presence of small quantities of carbon monoxide. The absorption vessel, containing the oil and a nickel catalyst, was connected to the gas-measuring tube by rubber tubing, and was adjusted so that the contents could be continuously and thoroughly shaken during the progress of the absorption.

Comparative experiments with pure hydrogen and with hydrogen containing from 0·25 to 2% of carbon monoxide show that the rate of hydrogenation is very considerably reduced by these quantities of carbon monoxide. The curve obtained by plotting the hydrogen absorption for a given interval of time against the percentage of carbon monoxide in the hydrogen is convex towards the origin, indicating that the retarding influence of successive increments in the carbon monoxide content decreases with increase in the quantity of the poisonous gas.

Apart from the poisoning effect of the carbon monoxide, the admixture of this gas dilutes the hydrogen, but this effect can be readily calculated and allowed for. H. M. D.

**Hydrogenation under the Influence of Colloidal Catalysts and how to account for this Process.** J. Böeseken and H. W. Hofstede (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 424—434).—The question of the mechanism of colloidal metal catalysts in hydrogenation processes is discussed and the results of observations are recorded on the rate at which hydrogen is absorbed by solutions of cinnamic acid, cinnamic esters, and ethyl undecenoate in presence of colloidal palladium. These results are not sufficiently regular to admit of mathematical treatment, and the authors infer that the normal course of the reaction is disturbed by impurities in the hydrogen, by coagulation of the catalyst, and by other unknown factors. [See *J. Soc. Chem. Ind.*, 1918, March.] H. M. D.

**The Fundamental Values of the Quantities $b$ and $\sqrt{a}$ for different Elements in Connexion with the Periodic System. V. The Elements of the Carbon and Titanium Groups.** J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 492—504. Compare A., 1916, ii, 386, 610; 1917, ii, 67).—The methods previously described have been applied to the calculation of the values of $b$ and $\sqrt{a}$ for the elements of the carbon and titanium groups. The critical data for these elements are, of course, not known, but the values of $b$ can be obtained from the compounds, for which in certain cases the requisite data are available. The chief result to which the author's calculations lead is that the value of $\sqrt{a}$ must be very large, ranging from 0·32 for carbon to 0·40 for lead. This is supposed to indicate that the attractive forces measured by $\sqrt{a}$ are those of the free atoms.

The estimated values of $\sqrt{a}$ and $b$ and also of the critical temperature and pressure are recorded in tables. H. M. D.

**The Fundamental Values of the Quantities $b$ and $\sqrt{a}$ for different Elements in Connexion with the Periodic System. VI. The Alkali Metals.** J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 505—519. Compare preceding abstract).—An attempt is made to estimate the values of $b$ and $\sqrt{a}$ for the alkali metals, the approximate value of the critical temperature required in the calculations being derived from the melting points and boiling points. The physical properties of the alkali metals necessitate the assumption of high values for the attraction constant, and this is assumed to be connected with the existence of these elements in the atomic condition. The estimated values of the critical data and of $b$ and $\sqrt{a}$ are recorded in tabular form. H. M. D.

**Considerations on the Nature of Chemical Affinity and of the Valency of Atoms** G. CIAMICIAN and M. PADOA (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 165—173).—The bearing of the results of recent work on the structure of the atom and on valency is discussed. T. H. P.

**Vacuum Balance Cases.** BERTRAM BLOUNT and WILLIAM H. WOODCOCK (T., 1918, **113**, 81—84).—Attempts have been made to construct a vacuum balance case of gun-metal. On account of the porosity of the metal, it was not found possible to reduce the rate of leakage much below that represented by 0·01 mm. per hour.

Better results were obtained with a glass case consisting of a large bell-jar with a side tubulus, through which the rider is controlled by an arrangement which is commonly made use of in the ordinary glass hypodermic syringe. A balance case constructed on these lines has been found to give satisfactory results. By means of a Gaede pump it can be exhausted to 0·001 mm. and the vacuum can be maintained for more than an hour. H. M. D.

**Method for Preventing Salts from Creeping over the Sides of Evaporating Dishes.** W. O. ROBINSON (*J. Amer. Chem. Soc.*, 1918, **40**, 197).—Creeping of salts can be prevented by painting a strip, about 6—7 mm. wide, round the inner rim of the dish with collodion. The film contains no non-volatile residue and can be easily burnt off. H. M. D.

**Lecture Experiment on the Vapour Pressure of Solutions.** H. S. VAN KLOOSTER (*J. Amer. Chem. Soc.*, 1918, **40**, 193—195). —A simple apparatus is described for demonstrating the lowering of the vapour pressure of a volatile liquid on the addition of a foreign non-volatile substance. It consists of an outer glass tube, in which the pure liquid is boiled, and an inner tube containing the solution. The inner tube is constricted somewhat about the middle of its length, and at its lower end is sealed on to a narrow tube, which is bent round to form a **U** with the wider tube, and is used as a gauge tube. The constriction serves to close the inner tube, when all the air has been removed, and this is conveniently effected by a rubber cork attached to a glass rod. When the outer tube is closed and the liquid boils,, vapour passes through the solution viâ the gauge tube, and when the air has been displaced the inner tube is closed by the rubber stopper. The level of the solution in the gauge tube is then found to be less than that in the wider tube. H. M. D.

**Preparation of Argon as a Lecture Experiment.** W. P. JORISSEN (*Chem. Weekblad*, 1917, **14**, 1151—1153).—A descriptoin of an apparatus for demonstrating the extraction of argon from air, the oxygen being absorbed by phosphorus, and the nitrogen by a mixture of magnesium-powder, fresh quick-lime, and sodium. A. J. W.

## Inorganic Chemistry.

**The Crystalline System and the Axial Ratio of Ice.** F. RINNE (*Ber. K. Sachs. Ges. Wiss. Math-phys. Klasse*, 1917, **69**, 57—62; from *Chem. Zentr.*, 1917, ii, 671. Compare *ibid.*, i, 452).—Using the apparatus described earlier, the statement of Nordenskiöld that ice is hexagonal–bipyramidal (hexagonal–hemimorphic, $a:c=1:1{\cdot}6$) is confirmed. This result is regarded as supporting the author's law of isotypism, according to which ice follows the magnesium type. D. F. T.

**Black Phosphorus. II.** A. SMITS, G. MEYER, and R. TH. BECK (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 392—393. Compare A., 1916, ii, 185).—Experiments in which black and violet phosphorus were heated for prolonged periods at 480° and 450° indicate that the black modification is metastable at these temperatures, and in presence of 1% of iodine as catalyst is transformed into the violet form. Mixtures of violet and black phosphorus in the ratio 4:1 heated for fourteen weeks at 380° showed complete transformation of the black into the violet form, but no appreciable change took place when the proportion of violet to black was 1:4. [See *J. Soc. Chem. Ind.*, 1918, March.] H. M. D.

**The Thermal Dissociation of Metaphosphoric Acid.** D. BALAREFF (*Zeitsch. anorg. Chem.*, 1918, **102**, 34—40).—The author studies the formation and thermal dissociation of metaphosphoric acid by heating orthophosphoric acid for varying lengths of time in a pear-shaped gold flask having a long neck. A current of dry air, led into the flask through a gold tube, serves to carry away any water-vapour formed, whilst the volatilised metaphosphoric acid and phosphoric oxide condenses in the neck of the flask. At the end of an experiment the flask is closed, weighed, and the residue analysed by estimating phosphoric oxide by the method of Schmitz. The product always contains less water than that required for metaphosphoric acid, the deficiency being greater the more prolonged the heating. The thermal dissociation of metaphosphoric acid in the gaseous state is therefore established. The results of those observers who have obtained metaphosphoric acid containing excess of water are to be explained by insufficient heating or by the presence of impurities in the phosphoric acid used (compare Holt and Myers, T., 1913, **103**, 532—536). The dehydration of orthophosphoric acid solutions by heating does not take place in definite

stages, but is influenced by the rate of heating and by the vapour tensions of water and phosphoric oxide. Even at 260—300° phosphoric acid volatilises with the water in appreciable quantities. The composition of the residue depends on the temperature and duration of heating. [Compare *J. Soc. Chem. Ind.*, 1918, March.]
E. H. R.

**The Existence of Basic Calcium Carbonates.** ED. DONATH and A. LANG (*Österr. Chem. Zeit.*, 1917, [ii], **20**, 175—176; from *Chem. Zentr.*, 1917, ii, 672).—When brought into contact with water and lime, calcium carbonate becomes hardened, due to a fixation of part of the lime; this result is adduced as evidence of the probable existence of basic carbonates of calcium (compare Busvold, A., 1917, ii, 207). D. F. T.

**Glucinum Nitride.** A. C. VOURNASOS (*Bull. Soc. chim.*, 1917, [iv], **21**, 282—288. Compare A., 1911, ii, 600; 1913, i, 25).—Glucinum nitride may be obtained by the direct action of cyanogen on glucinum at 800°.

The partial oxidation of a cyanide or of a carbide in the presence of nitrogen will in certain cases yield nitrides. Thus if zinc or copper cyanide or calcium carbide is heated with ammonium nitrate, the corresponding nitride is formed: $3Zn(CN)_2 + 12NH_4NO_3 = Zn_3N_2 + 6CO_2 + 14N_2 + 24H_2O$. Barium cyanamide similarly reacts with ammonium nitrate to give barium nitride. [See also *J. Soc. Chem. Ind.*, 1918, March.] W. G.

**A Silica-Glass Mercury Still.** J. C. HOSTETTER and R. B. SOSMAN (*J. Washington Acad. Sci.*, 1918, **8**, 11—15).—Vacuum mercury stills made of ordinary or combustion glass are liable to collapse when slightly overheated. This has led to the construction of a silica-glass still, the design of which is of the simplest possible kind, in order to minimise the difficulties connected with the working of the fused silica. The distillation chamber is heated electrically and the pressure reduced to less than 10 mm. H. M. D.

**Mercury Ammonia Compounds. I.** MURIEL CATHERINE CANNING HOLMES (T., 1918, **113**, 74—79).—By digesting infusible precipitate at 100° with solutions nearly saturated with respect to ammonium chloride and containing varying quantities of mercuric chloride, and examining the crystals which separate on cooling, it has been found that the product consists of the compound $3HgCl_2,2NH_3$ or of $HgCl_2,2NH_3$. There is no evidence of the formation of any compound of intermediate composition.

The product obtained under similar conditions by using solutions nearly saturated with mercuric chloride and variable small amounts of ammonium chloride has the composition $HgCl_2,NH_2{\cdot}HgCl$. This compound has previously been obtained by Strömholm (A., 1906, i, 935; *Zeitsch. anorg. Chem.*, 1908, **57**, 72). H. M. D.

**Electrolysis of Solutions of the Rare Earths. III.** L. M. DENNIS and A. B. RAY (*J. Amer. Chem. Soc.*, 1918, **40**, 174—181). The fact that the electrolysis of solutions of rare earth salts leads to the fractional precipitation of the rare earth hydroxides (compare A., 1915, ii, 775) has been attributed to the action of the hydroxyl ions set free at the mercury cathode, the hydroxide of the weakest base being precipitated first. In the expectation that vigorous stirring of the mercury surface would facilitate the fractionation, experiments have been made with neutral solutions of the nitrates of the rare earths of the yttrium and erbium groups, the average atomic weight of the metal being 106·95. The hydroxides precipitated at different stages were removed and the average atomic weight of the metal in each fraction determined.

Comparing the results obtained in two series of electrolytes, in one of which the cathode was vigorously, and in the other slightly agitated, it is found that vigorous stirring causes a more rapid segregation of the earths of higher atomic weight in the early fractions and a better concentration of the earths of lower atomic weight in the last fractions.

Other experiments in which neutral solutions of the nitrates of the rare earths and thorium were electrolysed show that fractionation occurs, the thorium being concentrated in the early fractions. [See also *J. Soc. Chem. Ind.*, 1918, March.] H. M. D.

**A Thermoelectric Method for the Study of the Allotropic Transformations of Metals.** R. DURRER (*Stahl und Eisen*, 1917, **37**, 430—431; from *Chem. Zentr.*, 1917, ii, 672. Compare Benedicks, A., 1916, ii, 172).—After a description of the apparatus used by Benedicks, a statement is made that the decision of the latter with respect to the discontinuity at the point $A_3$ of the curve for iron and the absence of discontinuity at the point $A_2$ is based on insufficient material. D. F. T.

**Iso- and Hetero-poly Acids. XV. Heteropolytungstates and some Heteropolymolybdates.** ARTHUR ROSENHEIM and JOHANNES JAENICKE (*Zeitsch. anorg. Chem.*, 1917, **101**, 235—275. Compare this vol., 19).—In this paper is given the new experimental data which the authors have used in the development of their theory of the constitution of the heteropoly acids. The acids of the fundamental type have the constitution expressed by the formula $H_{12-n}[R^n(M_2O_7)_6]$, where R is the non-metallic element and M the metallic. These acids form two series of hydrates, one series crystallising in quadratic octahedra with $28H_2O$, the other in rhombohedra with $22H_2O$. They are the most stable of the heteropoly acids and are formed in presence of excess of the metallic acid. The 8- and 9-basic acids show isomerism of a type not understood.

12-*Borotungstic acid*, $H_9[B(W_2O_7)_6],28H_2O$, forms crystals of two kinds, large, transparent octahedra, m. p. 45—51°, and slender needles. A lower hydrate with $10H_2O$ was isolated. An *iso*-12-*borotungstic acid*, $H_9[B(W_2O_7)_6],22H_2O$, was obtained in the form of hexagonal, bipyramidal crystals.

12-*Silicomolybdic acid*, $H_8[Si(Mo_2O_7)_6],28H_2O$, forms transparent octahedra, which melt gradually at 47—55° to a uniform liquid.

Crystallised from hot nitric acid, it forms a lower hydrate with $14H_2O$.

12-*Silicotungstic acid* forms both quadratic and rhombohedral hydrates with $28H_2O$ and $22H_2O$ respectively. The transition point, determined by the dilatometer method, is at 28·5°. In addition, a hydrate with $15H_2O$ was obtained.

*Iso*-12-*silicotungstic acid*, $H_8[Si(W_2O_7)_6],20H_2O$, forms triclinic prisms.

12-*Phosphomolybdic acid* was obtained in yellow, octahedral crystals of the composition $H_7[P(Mo_2O_7)_6],28H_2O$, and by crystallisation from hot nitric acid the hitherto unknown hydrate with $22H_2O$ was obtained in small, yellow, probably rhombohedral tables. The conductivity at 25° was studied, and also the course of neutralisation by means of conductivity measurements.

12-*Phosphotungstic acid* forms crystals of the normal type with $28H_2O$. In presence of traces of acid these break down into minute rhombohedra of the hydrate with $22H_2O$, melting at 89—94° to a homogeneous liquid. The highest metallic salts which could be prepared were tribasic, for example, $Ba_3H_8[P(W_2O_7)_6]_2,54H_2O$ and $Na_3H_4[P(W_2O_7)_6],13H_2O$, but in the guanidine salt,

$$(CN_3H_5)_7H_7[P(W_2O_7)_6]_2,12H_2O,$$

half the hydrogen is replaced.

12-*Arsenotungstic acid* could only be obtained in the form of its ammonium salt, $(NH_4)_3H_4[As(W_2O_7)_6],4H_2O$.

The unsaturated mono-nucleic heteropoly acids are of the type $H_{12-n}[R^nO(M_2O_7)_5]$, their basicity being the same as that of the saturated acids.

10-*Silicotungstic acid* was obtained in the form of a potassium salt, badly formed, cube-like crystals of the composition

$$K_7H[SiO(W_2O_7)_5],11H_2O.$$

The corresponding guanidine salt contains $9H_2O$.

The bi-nucleic heteropoly acids form two groups, the 1 : 11 acids having an outer bridge,

$$H_7[R^n\cdot OH\cdot(M_2O_7)_5]\cdot M_2O_7,[R^n\cdot OH\cdot(M_2O_7)_5]H_7,$$

whilst the 1 : 9 (luteo) acids have an inner bridge,

$$H_{11-n}[(M_2O_7)_4R^nO\cdot M_2O_7\cdot R^nO\cdot(M_2O_7)_4]H_{11-n}.$$

The acids of the last type, it is suggested, are in tautomeric equilibrium with the form

$$H_{10-n}[(M_2O_7)_4R^nOH\cdot M_2O_7\cdot R^nOH(M_2O_7)_4]H_{10-n}.$$

They are always formed in presence of excess of the metalloid acid.

11-*Phosphotungstates* are formed at an intermediate stage in the decomposition of 12-phosphotungstic acid by strong bases. They are stable salts which can be readily prepared from the barium salt, to which the constitution

$$Ba_7[P(OH)(W_2O_7)_5]–W_2O_7–[(W_2O_7)_5(OH)P]53H_2O$$

is given. Strong mineral acids bring about decomposition of the 11-phosphotungstates with formation of 12- and 2 : 21-phosphotungstates. The 11-*arsenotungstates* are completely analogous to the corresponding phosphotungstates.

9-*Phosphotungstic acid*, $P_2O_5,18WO_3,42H_2O$, forms thin, six-sided tables, which are very readily soluble and melt at 28°. All attempts to prepare salts of higher basicity than 5 failed, and it is concluded that the constitution of the acid must be represented by the formula

$$H_5[P(OH)(W_2O_7)_4–W_2O_7–(W_2O_7)_4(OH)P]H_5,36H_2O.$$

A study of the conductivity and neutralisation curves points to the same conclusion.

The silver salt, $5Ag_2O,P_2O_5,18WO_3,34H_2O$, is precipitated as yellow, amorphous flakes which quickly crystallise. It is almost insoluble. The corresponding guanidine salt, with $18H_2O$, forms bright yellow aggregates of small tables and is only slightly soluble.

9-*Arsenotungstic acid* corresponds exactly with luteophosphotungstic acid. Only the tribasic potassium and ammonium salts were prepared, these having similar properties to the tribasic salts of 9-phosphotungstic acid.

Among the more complex heteropoly acids, the authors have studied 2:21-phosphotungstic acid, 2:17-phospho- and 2:17-arsenotungstic acids. They probably contain four non-metallic acid nuclei, but no constitutional formulæ have yet been suggested for them. The preparation and properties of a number of salts of these acids are described. E. H. R.

## Mineralogical Chemistry.

**Amblygonite-Tin Deposits at Caceres, Spain.** W. T. Dörpinghaus (*Jahrb. Min.*, 1917, i, Ref. 326—328; from *Archiv Lagerstättenforschung*, 1914, **16**, 49 pp.).—Veins containing amblygonite and cassiterite intersect Silurian and Devonian slates in the neighbourhood of the well-known phosphate veins of Estremadura. The average composition of the amblygonite is given under I. Associated minerals are pyrophyllite (anal. II) and a soda-muscovite (III).

| | $SiO_2$. | $P_2O_5$. | $SO_3$. | $Al_2O_3$. | $Fe_2O_3$. | CaO. | MgO. |
|---|---|---|---|---|---|---|---|
| I. | — | 46·35 | — | 34·29 | 0·79 | — | — |
| II. | 67·01 | trace | trace | 17·93 | 0·06 | — | — |
| III. | 45·78 | trace | 0·08 | 36·49 | 0·15 | 0·08 | 0·11 |

| | $K_2O$. | $Na_2O$. | $Li_2O$. | $H_2O$. | F. |
|---|---|---|---|---|---|
| I. | — | 1·60 | 8·87 | 5·16 | 3·00 |
| II. | 6·27 | 2·23 | — | 6·69 | — |
| III. | 8·41 | 3·25 | — | 5·15 | — |

L. J. S.

**Celestite from Galicia.** Stefan Kreutz (*Jahrb. Min.*, 1917, i, Ref. 269—277; from *Abh. Akad. Wiss. Krakau*, 1915, **55**, [*A*], 1—24).—An account is given of the minerals (aragonite, rock-salt, gypsum, celestite, calcite, and dolomite) found in the salt-clays which are worked for ozocerite and sulphur in the mining district of Pomiarki, near the village of Truskawiec in Galicia. A crystallographic description is given of the celestite; analysis gave:

| $SrO$. | $BaO$. | $CaO$. | $SO_3$. | Ign. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|
| 54·41 | 0·69 | 0·67 | 43·54 | 0·22 | 99·53 | 3·968 |

corresponding with $SrSO_4$ 97·38, $CaSO_4$ 1·64, $BaSO_4$ 0·98.

Mixed crystals of these sulphates are discussed, and the fact that the minerals celestite, barytes, and anhydrite always contain a predominance of one metal is commented upon. L. J. S.

**The Existence of Bischofite Deposits and the Secondary Transformations of the Zechstein Potassium Salts.** M. Rózsa (*Zeitsch. anorg. Chem.*, 1917, **101**, 276—284. Compare A., 1916, ii, 257, 335; 1917, ii, 97, 214).—Fresh arguments are put forward in support of the author's contention that bischofite did not form a primary deposit, and therefore could not have participated in the secondary metamorphoses of the salt deposits. The carnallite–kieserite salts of the 16 metres thick "principal" salt layers are the primary products. The mean composition of five borings through this deposit gave carnallite 56%, kieserite 13·3%, rock-salt 28·7%. The kieserite–carnallite layers are less rich in carnallite. The origin of this carnallite can be explained without the assumption of a primary bischofite deposit, on the supposition that the magnesium chloride appears as a decomposition product of the "principal" salt deposit.

The thermal or hydrothermal decomposition of kainite into kieserite and carnallite has been studied from the van't Hoff equilibrium diagram, and it is concluded from the relative proportions of these two salts in the "principal" salt deposits that the last could not have been produced by the decomposition of kainite. The occasional transformation of the "principal" deposits into a hard-salt rich in langbeinite can be explained qualitatively, but quantitative data are wanting. [See also *J. Soc. Chem. Ind.*, 1918, March.] E. H. R.

**Rock-forming Minerals from the Tatra Mountains.** W. Pawlica (*Jahrb. Min.*, 1917, i, Ref. 278—282; *Bull. Acad. Sci. Cracovie, Cl. sci. math. nat.*, [*A*], 1915, 52—76).—Thirteen detailed analyses are given of minerals (muscovite, biotite, orthoclase, oligoclase, amphibole, garnet, and tourmaline) isolated from granite, pegmatite, and gneiss. L. J. S.

## Analytical Chemistry.

**Accurate Method for taking Aliquots of a Standard in Standardising Solutions.** C. F. Miller (*J. Amer. Chem. Soc.*, 1917, **39**, 2388).—About five times as much of the standard substance is weighed out and dissolved in a quantity of water slightly exceeding five times the capacity of the pipette to be used in taking the aliquot portions. (This pipette need not be standardised.) Five portions of the solution are now pipetted into separate vessels, and the remainder of the solution, together with the rinsings from the pipette, is transferred to a tared platinum basin, evaporated, the residue dried, and weighed. A simple calculation gives the quantity of substance taken for each titration. The method can be used only for such substances as sodium carbonate, sodium oxalate, etc., which are soluble, and separate from their solution in a weighable form on evaporation. W. P. S.

**A General Method for the Analysis of Gaseous Mixtures.** PAUL LEBEAU and A. DAMIENS (*Ann. Chim.*, 1917, [ix], **8**, 221—264).—A more detailed account of work already published (compare A., 1913, i, 437; ii, 253, 349, 700). W. G.

**The McLean-Van Slyke Iodometric Method for the Titration of Small Amounts of Haloids. Its Application to Chlorides.** ROBERT F. MCCRACKEN and MARY D. WALSH (*J. Amer. Chem. Soc.*, 1917, **39**, 2501—2506. Compare A., 1915, ii, 479).—When the titration in this method is made very slowly, a blue coloration which might be mistaken for the end-point sometimes develops before the titration is complete; this coloration, however, disappears gradually as the end-point is approached. The end-point can be obtained in a clear solution by adding a further quantity of starch just before the titration is commenced. The method yields trustworthy results. [See, further, *J. Soc. Chem. Ind.*, 1918, 6A.] W. P. S.

**Applications of Gas Analysis. IV. The Haldane Gas Analyser.** YANDELL HENDERSON (*J. Biol. Chem.*, 1918, **33**, 31—38).—Modifications of Haldane's apparatus for the estimation of carbon dioxide in air and in blood are described, by means of which the apparatus may be more readily taken apart and cleaned. A simpler form of the apparatus suitable for teaching purposes is also illustrated. [See also *J. Soc. Chem. Ind.*, 1918, March.] H. W. B.

**Applications of Gas Analysis. V. The Gases of the Blood.** YANDELL HENDERSON and ARTHUR H. SMITH (*J. Biol. Chem.*, 1918, **33**, 39—46. Compare preceding abstract).—The authors describe a modification of Barcroft and Haldane's method, in which the oxygen from 1 c.c. of the blood is liberated by the action of potassium ferricyanide in a special "diffusion tube." which is subsequently rotated horizontally. During the rotation, the contents of the tube spread in a thin film along the walls and allow complete diffusion of the liberated oxygen into the air of the tube to occur. The excess of oxygen in the air is then estimated by means of the analyser previously described (*loc. cit.*). Carbon dioxide in the blood is similarly estimated after treatment with tartaric acid, a correction being made for the solubility of carbon dioxide in acidified solutions of blood. H. W. B.

**Gasometric Estimation of the Oxygen and Hæmoglobin of Blood.** DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1918, **33**, 127—132. Compare A., 1917, ii, 422).—The apparatus previously described for the estimation of carbon dioxide in the blood is used with a similar technique for the estimation of oxygen. The oxygen is liberated from combination with hæmoglobin within the apparatus by the addition of ferricyanide, is extracted in a vacuum, and measured at atmospheric pressure, a few minutes sufficing for an accurate estimation. H. W. B.

**Rapid Characterisation of the Sulphuric Ion in Insoluble Sulphates. Application to the Identification of this Ion in General.** G. DENIGÈS (*Bull. Soc. chim.*, 1918, [iv], **23**, 36—39).—The presence of the sulphuric ion in insoluble sulphates, such as those of lead, mercurous mercury, calcium, strontium, and barium, may readily be shown by adding to the sulphate a 10% solution of mercuric nitrate in nitric acid (1 in 100). Turpeth mineral is formed, and may be detected, if necessary, microscopically. Calcium and mercurous sulphates give the reaction immediately in the cold, strontium and lead sulphates only slowly, and barium sulphate only on boiling. In a complex mixture, the sulphate may be first precipitated as barium sulphate and then detected as described. [See also *J. Soc. Chem. Ind.*, 1918, March.] W. G.

**The Adaptation of Truog's Method for the Estimation of Carbon Dioxide to Plant Respiration Studies.** A. M. GURJAR (*The Plant World*, 1917, **20**, 288—293; from *Physiol. Abstr.*, 1918, **2**, 641).—In the original paper an apparatus is described for the estimation of carbon dioxide by Truog's method, the gas being absorbed in a known volume of *N*/4-barium hydroxide solution, and the residual hydroxide titrated back with standard acid. The modification consists in the use of an automatic pipette for measuring and transferring the barium hydroxide solution without allowing it to come into contact with the air. There is also an arrangement for rendering the wash-water free from carbon dioxide without disconnecting the reservoir. W. G.

**Use of Sodium Paratungstate in the Estimation as Oxide of the Metal in Cyanides.** S. B. KUZIRIAN (*J. Amer. Chem. Soc.*, 1917, **39**, 2356—2358. Compare A., 1913, ii, 865).—Cyanides, when heated with sodium paratungstate in the presence of an oxidising substance (ammonium nitrate) lose their acid radicle, leaving a residual oxide in a definite and stable form for weighing together with the paratungstate. [See, further, *J. Soc. Chem. Ind.*, 1918, 30A.] W. P. S.

**Estimation of Sodium and Potassium.** F. H. MCCRUDDEN and C. S. SARGENT (*J. Biol. Chem.*, 1918, **33**, 235—241).—Sodium and potassium are separated from other compounds as the combined chlorides, and the amount of each is calculated from the chlorine content of a known weight of the mixture. The authors show that when the McLean-Van Slyke method is employed for estimating the chlorine, the probable error in the estimation of the sodium increases as the ratio of sodium to potassium decreases, and amounts usually to about 1%. H. W. B.

**New Hydrogen Electrode for the Electrometric Titration of the Alkaline Reserve of Blood Plasma and other Frothing Fluids.** J. F. McClendon (*J. Biol. Chem.*, 1918, **33**, 19—29).—The new electrode vessel is attached to a horizontal spindle in such a way as to permit the introduction at the free end of acid and of hydrogen during rotation without disconnection from the potentiometer. The addition of $N/10$-hydrochloric acid to the plasma is continued until the hydrogen-ion concentration is that of water ($pH = 7\cdot00$ at 23°). The amount of acid required is a measure of the alkaline reserve of the blood. H. W. B.

**Volumetric Method for the Estimation of Calcium.** J. Grossfeld (*Chem. Zeit.*, 1917, **41**, 842).—The calcium is precipitated from a solution slightly acidified with phosphoric acid by the addition of a definite quantity of ammonium oxalate, the calcium oxalate is then separated by filtration through a "kieselguhr filter-paper," and the excess of ammonium oxalate is titrated, with permanganate, in an aliquot portion of the filtrate. [See, further, *J. Soc. Chem. Ind.*, 1918, 76A.] W. P. S.

**Identification and Estimation of Lead in Water.** Robert Meldrum (*Chem. News*, 1918, **117**, 49—50).—In the colorimetric estimation of lead by means of hydrogen sulphide, it is essential that the standard or comparison solution be prepared with the same water free from lead. The colouring matter in the water and the proportion of saline constituents influence the intensity of the coloration due to lead sulphide, the difference in some cases amounting to 100%. When distilled water is used for the standard solution, the lead may be underestimated to the extent of 33%. [See, further, *J. Soc. Chem. Ind.*, 1918, March.] W. P. S.

**A New Method of Estimating Copper.** James Moir (*J. Chem., Met., Min. Soc. S. Africa*, 1917, **18**, 133—135).—The sample is dissolved in concentrated nitric acid and the copper converted into faintly acid cupric acetate either by the usual method or by adding carbamide, boiling, nearly neutralising with sodium hydroxide, and adding sodium acetate. A slight excess of sodium thiosulphate is added to the solution, followed immediately by an excess of potassium thiocyanate. The precipitated copper thiocyanate is filtered through filter-pulp and washed, the filtrate is diluted, sulphuric acid and a small quantity of starch solution are added, and the excess of thiosulphate is titrated with $N/10$-iodine solution. [For details, see *J. Soc. Chem. Ind.*, 1918, March 15th.] T. F. B.

**Colorimetric Estimation of Manganese by Oxidation with Periodate.** HOBART H. WILLARD and LUCIEN H. GREATHOUSE (*J. Amer. Chem. Soc.*, 1917, **39**, 2366—2377).—Manganese salts are readily oxidised to permanganate by heating with an alkali periodate in acid solution. The quantity of free sulphuric acid present must be sufficient to prevent the precipitation of manganic periodates or oxides; a high concentration of acid, prolonged heating, and the presence of ammonium salts are without effect on the results. Traces of chloride do not interfere, and the common metals, if they do not form coloured ions, may be present. Reducing substances must be removed previously by treatment with nitric acid; phosphoric acid should be added if much iron is present. The quantity of permanganate formed is estimated colorimetrically. [See, further, *J. Soc. Chem. Ind.*, 1918, 41A.]

W. P. S.

**Use of Cupferron (Ammonium Salt of Nitrosophenylhydroxylamine) in: I. The Quantitative Separation of Zirconium, Titanium, Iron, Manganese, and Aluminium. II. The Analysis of Zircon and Baddeleyite.** JAMES BROWN (*J. Amer. Chem. Soc.*, 1917, **39**, 2358—2366. Compare Thornton and Hayden, A., 1914, ii, 779).—Cupferron reagent may be used for the precipitation and separation of iron, titanium, and zirconium from aluminium and manganese. The precipitation is made from a sulphuric acid solution. The iron, titanium, and zirconium are then separated from one another by the use of standard methods, and the aluminium and manganese are estimated after the excess of cupferron has been destroyed by treatment with concentrated nitric acid. The method yields trustworthy results either with mixtures of the pure salts or with minerals containing the elements mentioned. [See, further, *J. Soc. Chem. Ind.*, 1918, 41A.]

W. P S.

**Reagents for Use in Gas Analysis. VII. The Estimation of Benzene Vapour.** R. P. ANDERSON (*J. Ind. Eng. Chem.*, 1918, **10**, 25—26).—A method is proposed for the estimation of benzene vapour in gas in which a measured quantity of gas containing benzene vapour is placed in contact with benzene in a special apparatus, and the increase in volume read. By determining what the increase would have been had there been no benzene vapour present, the amount of benzene vapour present can be estimated. A standard apparatus has not yet been produced.

L. A. C.

**Estimation of Phenol in the Presence of the Three Cresols.** G. W. KNIGHT, C. T. LINCOLN, G. FORMANEK, and H. L. FOLLETT (*J. Ind. Eng. Chem.*, 1918, **10**, 9—18).—From a series of determinations of the specific gravities and solidifying points of a number of mixtures of pure phenol and pure *o*-, *m*-, and *p*-cresols, the authors have devised a method for determining the percentage of phenol present in unknown mixtures of these compounds.

Details are given for carrying out the method and obtaining the necessary measurements for solving the equation:

$$\text{Per cent. phenol} = 100X\,[(T_o - T_{so})(0{\cdot}366 + 0{\cdot}702L_s) + (G_{so} - G_o)(2970 - 609L_s)]/30\,W.$$

where $L_s = \{1000(G_p - G_{sp})\}/\{T_p - T_{sp}\} - 0{\cdot}842$; $G_p$ and $G_{sp} = \mathrm{D}^{45}_{45}$ of phenol used and phenol + distillate mixture respectively; $G_o$ and $G_{so} = \mathrm{D}^{25}_{25}$ of *o*-cresol used and *o*-cresol + distillate mixture respectively; $T_p$, $T_{sp}$, $T_o$, and $T_{so}$ = solidifying points of the phenol, phenol + distillate mixture, *o*-cresol used and *o*-cresol + distillate mixture respectively; $X$ = wt. of total distillate below 197°; $W$ = wt. of sample used.

This equation does not give absolutely accurate results with all possible mixtures of the three isomerides, or where both *o*-cresol and *m*-cresol are present and *p*-cresol is absent or present only in very small quantities, the results in this case being too low. The error increases as *o*-cresol increases and *p*-cresol decreases, being greatest where *p*-cresol is absent and more than 50% of *m*-cresol and less than 50% of *o*-cresol is present. In all cases ordinarily met with in commercial practice, however, the probable error would amount to only a few tenths per cent. [See, further, *J. Soc. Chem. Ind.*, 1918, 85A.] L. A. C.

**Estimation of Pentose in Urine.** G. TESTONI (*Policlinico*, 1917, **24**, 641; from *Physiol. Abstr.*, 1918, **2**, 598).—Ten c.c. of urine are decolorised by heating with blood charcoal and filtered. The filtrate is evaporated to 5 c.c., and to it is added 9 c.c. of a warm 0·25% solution of phloroglucinol in glacial acetic acid and 1 c.c. of hydrochloric acid. The mixture is allowed to remain at 50° for half an hour, when the characteristic colour will have appeared. A quantitative estimation may be made by means of a colorimeter. The method is applicable to diabetic urine. If pentose is the only sugar present, the filtrate from the decolorising process need not be evaporated. W. G.

**Estimation of Dextrose in Urine.** J. J. GURTOV (*Med. Record, New York*, 1917, **92**, 502—503; from *Physiol. Abstr.*, 1917, **2**, 497—498).—If a solvent (potassium ferricyanide) is added to the copper solution in amount less than is necessary to dissolve all the cuprous oxide, the reagent will remain clear until all the cyanide has combined with the greater part of the oxide; then a bulky precipitate occurs, and this sign of the end of the reaction is easily recognised. G. B.

**A Rapid Method for the Estimation of Sugar in Urine.** OTTO MAYER (*Münch. med. Woch.*, 1917, **64**, 1222—1223; from *Chem. Zentr.*, 1917, **2**, 653—654).—A mixture of 10 c.c. of the urine with 10 c.c. of 15% sodium hydroxide solution is diluted to 50 c.c. with water, and a 2·5% solution of copper sulphate gradually added, with shaking, until the precipitate has almost entirely redissolved and a just perceptible permanent turbidity remains, which increases somewhat on keeping. Under these conditions, each c.c. of the copper sulphate is equivalent to 0·1% of dextrose. If the urine contains more than 4% of dextrose, only 5 c.c. should be used, whilst if less than 0·5—1% is present, 20 c.c. should be taken. Should the urine give a precipitate of calcium phosphate, it should be previously treated with a measured proportion of sodium hydroxide solution, and a suitable fraction of the filtrate submitted to the above titration. Very turbid urines should be filtered, and excessive quantities of albumin removed by boiling before a sample is submitted to the above analytical process.

D. F. T.

**Acidosis. VII. Estimation of β-Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Urine.** DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1917, **32**, 455—493).—Dextrose and other interfering substances are first removed by treating 25 c.c. of the urine in a 250 c.c. measuring flask with 100 c.c. of water, 50 c.c. of a 20% copper sulphate solution, and, after mixing, 50 c.c. of 10% suspension of calcium hydroxide in water. After shaking and testing with litmus (if not alkaline, more calcium hydroxide is added), the mixture is diluted to the mark and allowed to remain for at least one-half hour for dextrose to precipitate. It is then filtered through a dry filter paper.

To estimate the total acetone substances, 25 c.c. of the urinary filtrate are placed in a 500 c.c. flask and boiled with 100 c.c. of water, 10 c.c. of 50% sulphuric acid, and 35 c.c. of 10% mercuric sulphate (73 grams of pure red mercuric oxide dissolved in 1 litre of 4*N*-sulphuric acid) under a reflux condenser. After boiling has begun, 5 c.c. of a 5% solution of potassium dichromate are added, and the boiling continued for one and a-half hours. The yellow precipitate which forms consists of an acetone–mercury–sulphate–chromate compound, and it is collected on a tared Gooch crucible, washed with 200 c.c. of cold water, and dried for an hour at 110°. After cooling in the air, it is weighed, or the precipitate may be dissolved in hydrochloric acid and titrated with standard potassium iodide solution.

The acetone plus the acetoacetic acid is estimated exactly as the total acetone substances, except that (1) no dichromate is added, and (2) the boiling is continued for not less than thirty and not more than forty-five minutes. The hydroxybutyric acid may be estimated separately by first acidifying with sulphuric acid and boiling off the acetone and acetoacetic acid. The factors for calculating the results are 1 mg. acetone yields 20 mg. of precipitate and 1 mg. hydroxybutyric acid yields 8·45 mg. of precipitate. In acetonuria, hydroxybutyric acid usually represents 75% of the total acetone substances.

H. W. B.

**Acidosis. VIII. Estimation of β-Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Blood.** DONALD D. VAN SLYKE and REGINALD FITZ (*J. Biol. Chem.*, 1917, **32**, 495—497. Compare preceding abstract).—The proteins are first removed by precipitation with mercuric sulphate, and the acetone substances are then estimated in the resulting filtrate exactly as described for urine (*loc. cit.*). H. W. B.

**A Biological Colour Reaction for Succinic Acid.** T. THUNBERG (*Svenska Läkareförenigenshandlingar*, 1917, **43**, 996—1001; from *Physiol. Abstr.*, 1918, **2**, 655. Compare this vol., i, 140).—The amount of succinic acid in tissues may be estimated as follows. The organ is extracted with amyl alcohol, and this is then extracted with ether. The ethereal extract is neutralised and its decolorisation effect in a solution containing methylene-blue and muscle is observed. By this means, 0·02 mg. of succinic acid can be detected and estimated. W. G.

**The Test for Tartrates Depending on the Formation of the Copper Tartrate Complex.** L. J. CURTMAN, A. LEWIS, and B. R. HARRIS (*J. Amer. Chem. Soc.*, 1917, **39**, 2623—2630).—The test for tartrates, which depends on the solubility of cupric hydroxide in alkaline solutions of the alkali tartrates, has been submitted to examination with the object of determining its sensitiveness. By the use of potassium ferrocyanide instead of ammonia for the detection of the dissolved copper in the filtered solution, it has been found possible to detect 0·2 mg. of tartrate.

Solutions which contain ammonium salts, arsenites, borates, or phosphates give a positive reaction in the absence of tartrates. Chromates, ferrocyanides, and ferricyanides interfere by masking the test colour, whilst cyanides readily dissolve cupric hydroxide. One mg. of tartrate gives a negative result in the presence of 500 mg. of thiosulphate, arsenate, chromate, fluoride, thiocyanate, nitrite, or acetate and also in the presence of 250 mg. of thiosulphate, oxalate, thiocyanate, or nitrite. Many organic substances interfere with the application of the test. H. M. D.

**Comparison between the Bromide-Bromate Method and the Methods of Hübl and of Wys for the Estimation of the Iodine Number of Oils and Fats.** C. KELBER and H. RHEINHEIMER (*Arch. Pharm.*, 1917, **255**, 417—424).—All three methods give concordant results for oils and fats having small iodine numbers, including hydrogenised oils which before hardening had large iodine numbers but have been extensively saturated by the addition of the hydrogen. The bromide–bromate method always gives too low results in the case of oils having large iodine numbers. The authors prefer the method of Wys to that of Hübl.

C. S.

**A Method for the Estimation of Uric Acid in Small Quantities of Blood, Urine, and other Body Fluids.** A. KOWARSKY (*Berlin Klin. Woch.*, 1917, **54**, 987—989; from *Physiol. Abstr.*, 1918, **2**, 586).—Proteins are first completely precipitated and removed, and the filtrate is concentrated to 2 c.c. The uric acid is precipitated by ammonium chloride, and the ammonia in the precipitate estimated by the formalin method. Accurate results are reported. W. G.

**Estimation of Phytin Phosphorus in Plant Products.** J. B. RATHER (*J. Amer. Chem. Soc.*, 1917, **39**, 2506—2515).—The ferric chloride titration method described by Heubner and Stadler (A., 1914, ii, 690) may be applied to the estimation of phytin in vegetable substances. Maximum extraction of the phytin phosphorus is attained by extraction with 1·2% hydrochloric acid for three hours. Non-phosphorised substances and phosphorus compounds other than phytin do not interfere with the estimation. The largest amount of phytin phosphorus was found in wheat bran, rice bran, rice polish, and cotton-seed meal (0·76 to 1·26%), and the smallest in maize, oats, soja beans, and clover seed (0·19 to 0·36%). [See, further, *J. Soc. Chem. Ind.*, 1918, 17A.] W. P. S.

**The Simplest and most Convenient Method for the Detection of Albumin in Urine.** F. LENZ (*Münch. Med. Woch.*, 1917, **64**, 1267; from *Physiol. Abstr.*, 1918, **2**, 613).—In this method only one reagent, namely, sulphosalicylic acid, is used, and heat is not necessary. W. G.

**Colorimetric Estimation of Hæmoglobin.** WALTER W. PALMER (*J. Biol. Chem.*, 1918, **33**, 119—126).—The blood is obtained in the usual manner, by pricking the finger or lobe of the ear. It is diluted by drawing 0·05 c.c. into a special pipette and transferring into 5 c.c. of 0·4% ammonium hydroxide solution contained in a test-tube. After rinsing out the blood pipette by drawing the ammonium hydroxide solution into it two or three times, ordinary illuminating gas is bubbled rapidly through the ammonia–blood solution for thirty seconds. It is then compared in a Duboscq colorimeter with a standard carbon monoxide hæmoglobin solution set at 10. For the preparation of the standard solution, a quantity of human or ox blood is obtained, and its oxygen capacity estimated (compare Van Slyke, this vol., ii, 82). The blood is diluted with 0·4% ammonium hydroxide solution, so as to make a 2% solution of a blood with an oxygen capacity of 18·5%, and it is then saturated with carbon monoxide. This stock solution will keep for many months, and the standard solution can be prepared from it at any time by diluting 5 c.c. to 100 c.c. with 0·4% ammonium hydroxide solution. The accuracy of the estimation is usually within 1%. [See also *J. Soc. Chem. Ind.*, 1918, March.] H. W. B.

# General and Physical Chemistry.

**Drude's Theory of Dispersion from the Point of View of Bohr's Model and the Constitution of $H_2$, $O_2$, and $N_2$.** A. Sommerfeld (*Ann. Physik,* 1917, [iv], **53**, 497—550).—A theoretical paper in which the author discusses the question of the dispersion and magnetic rotation of gases on the assumption that the structure of the molecules is in accordance with Bohr's hypotheses. The theoretical considerations are applied to hydrogen, oxygen, and nitrogen, for which certain structures are assumed, and the calculated refractive, dispersive, and magnetic rotatory powers are compared with those found by experiment. H. M. D.

**The Spectra of Isotopes and the Vibration of Electrons in the Atom.** William D. Harkins and Lester Aronberg (*Proc. Nat. Acad. Sci.*, 1917, **3**, 710—714).—The wave-length of the line $\lambda$ 4058 in the spectra of ordinary lead and of lead from radium (radium-*G*) has been measured with great accuracy by the use of a 10-in. plane grating, giving a sixth order spectrum with a dispersion of 0·359 Å. per mm. The atomic weight of the specimen of radium-*G* employed had been found by Richards to be 206·34, compared with 207·18 for ordinary lead.

In order to avoid mechanical shifts, the two spectra were photographed simultaneously, the vacuum arc lamps employed as sources of light being interchanged from time to time during the taking of the records. In all, seventeen experiments were made, and the plates show in all cases that the wave-length of the line $\lambda$ 4058 in the spectrum of radium-*G* is greater than it is in ordinary lead, the average difference being equal to 0·0043 Å

The observations are said to establish definitely the existence of a measurable difference between the wave-lengths of corresponding lines in the spectra of isotopes. The photographs indicate clearly that the shift is real and cannot be explained by broadening. H. M. D.

**Arc Spectrum of Gadolinium.** Josef Maria Eder. (A communication from *Photochem. Lab. d. K. K. Graph. Lehr- u. Versuchsanstalt Wien,* 1467—1535; from *Chem. Zentr.*, 1917, ii, 362).—The author has investigated this spectrum with the aid of gadolinium products obtained by Auer by a fractionation which separated gadolinium from samarium and europium. The chloride gives a purer spectrum than the oxide. The tables of gadolinium lines measured occupy 62 quarto pages. The fractions containing europium prepared by Auer give indications spectroscopically of the presence of an unknown element lying between europium and samarium. R. V. S.

**The Spectrum of Nickel.** J. E. Paulson (*Physikal. Zeitsch.* 1918, **19**, 13—15).—An examination of the wave-lengths of lines,

In cross references to abstracts *Ind.* will be used in place of *J. Soc. Chem. Ind.*, 1918, **37**.

in the arc spectrum of nickel has shown the existence of thirty-three groups of eight lines with constant differences between the corresponding wave-numbers. The lines in question are tabulated and the relative intensities are shown. H. M. D.

**The Ultimate Rays of Great Sensitiveness of Columbium and Zirconium.** A. DE GRAMONT (*Compt. rend.*, 1918, **166**, 365—368).—Under the conditions previously described for titanium (compare this vol., ii, 49), the ultimate rays of columbium which could be detected photographically were λ=4101·0, 4079·7, 4059·0. None of these was visible to the eye at dilutions much above 1:100. The ultimate rays of zirconium were λ=3496·2, 3438·2, 3392·0. The sensitiveness of the group of five rays in the blue, Zr*a*, was small. W. G.

**Resonance Spectra of Iodine.** R. W. WOOD (*Phil. Mag.*, 1918, [vi], **35**, 236—252. Compare A., 1913, ii, 994; 1914, ii, 233). —An account is given of further observations on the resonance spectra which are emitted by iodine vapour when this is excited by the light from a Cooper-Hewitt mercury lamp. An improved method of illumination is described.

The doublet series, which is excited by the green mercury line, has been found to extend towards the red end of the spectrum up to λ 7685. The photographs, obtained by means of plates sensitised with dicyanine, show most of the doublets of the series, the last doublet at λ 7685 being of the twenty-seventh order. It is probable that this represents the limit of the resonance spectrum, for the plates used were highly sensitive to beyond λ 8500. The position of the twenty-seventh order doublet is, moreover, approximately the same as the limit of the absorption spectrum.

If the plates are exposed to the resonance radiation for longer periods, the doublets are found to be accompanied by faint companion lines, some of which may be due to excitation by the satellites of the green mercury line, but the author considers that some are to be attributed to the stimulating influence of the green line itself. On greatly prolonged exposure, it is found that the doublets fuse together to form a series of wide bands. If a gas of the helium group is introduced into the iodine tube, the intensity of the doublets is greatly reduced, and a series of fluted bands makes its appearance. These bands, which occupy positions between the doublets, are not exhibited by the resonance spectrum of iodine in a vacuum. It is probable that the lines forming the doublets are themselves constituents of the fluted bands, and that the appearance of the bands in presence of an inert gas is due to a transfer of energy from one part of the vibrating system to another as a result of collisions between iodine molecules and molecules of the inert gas. It may in this way be possible to account for the complicated system of bands in the absorption spectrum, these bands being referred to simpler systems which can be excited separately.

If the iodine vapour in a vacuum is excited by means of a quartz mercury arc, complicated groups of lines are obtained in place of the doublet series. This is attributed to the circumstance that, under these conditions, the green mercury line has broadened to such an extent that it covers a number of the iodine absorption lines. The intensity distribution amongst the groups of lines produced by this multiplex excitation is approximately the same as the distribution in the doublet series. The complexity of the groups increases with the width of the green exciting line.

A short reference is made to the resonance spectra excited by the two yellow mercury lines, but these have not yet been examined in detail. H. M. D.

**Series Law of Resonance Spectra.** R. W. Wood and M. Kimura (*Phil. Mag.*, 1918, [vi], **35**, 252—261. Compare preceding abstract).—The wave-lengths of lines in the resonance spectra of iodine are recorded and the law of distribution is discussed.

The series of strong doublets excited by the green line of the Cooper-Hewitt lamp has been examined with particular care, with the result that the frequency difference between the components is found to be constant and equal to 50. The spacing of the first member (shorter $\lambda$ component) of each doublet is represented by the formula $1/\lambda_m = 183075 - 2131{\cdot}414 + 12{\cdot}734m(m-1)/2$, in which $\lambda_m$ is the wave-length of the first member of the doublet of the $m$th order. The agreement between the calculated and observed values is quite good up to the doublet of the fifteenth order, but as the order becomes greater the divergence increases.

Other series of doublets with constant frequency differences may be approximately represented by a similar formula.

The lines in the resonance spectrum excited by the yellow lines $\lambda$ 5769·6 and $\lambda$ 5790·7 have also been examined with reference to the law of distribution. The doublets in these groups of lines are not characterised by the same regularities as those in the groups excited by the green mercury line. The frequency difference between the components has not a constant value, but the spacing of the doublets in the groups of lines excited by the yellow line $\lambda$ 5769·6 is such that the difference between the successive values of $1/\lambda$ is nearly constant. The degree of constancy is not so pronounced for the case of the groups which are excited by $\lambda$ 5790·7.

H. M. D.

**Absorption Spectrum of Oxyhæmoglobin in the Ultra-violet and Extreme Ultra-violet Regions.** Toshikazu Mashimo (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 199—202).—Oxyhæmoglobin, purified by crystallisation, was dissolved in water and the photographic records obtained by interposing layers of this solution, varying in thickness in the ratio of the integral numbers from 1 to 42, between a carbon arc and the photographic plate, are compared. These records show an absorption band with the centre at $\lambda$ 350 $\mu\mu$, which is possibly the same as that described by Peyrega and Vlès as occurring at λ 333 $\mu\mu$ (*Compt. rend.*, 1912, **154**, 133). No absorption could be detected in the Schumann region.

H. M. D.

**The Fluorescence of Cyano-compounds.** HUGO KAUFFMANN (*Ber.*, 1917, **50**, 1614—1623).—See this vol., i, 113.

**Rotation Inversion and Anomalous Rotation Dispersion.** HERMANN GROSSMANN and MARIE WRESCHNER (*J. pr. Chem.*, 1917, [ii], **96**, 125—165).—The dextrorotatory power of tartaric acid in aqueous solution is probably due to the dissociation of the acid, because with increasing concentration of the solutions the rotation falls, and, indeed, the molten or solid acid is lævorotatory. Addition of acids such as hydrochloric or nitric acid to the aqueous solution depresses the dissociation, the normal rotatory dispersion curve which rises from red to violet becoming gradually altered by an increasing proportion of added acid until a falling curve results; during the inversion of the nature of the curve the latter exhibits a maximum, which gradually moves in the direction of increased wave-length as the concentration of added acid is raised. Acetic acid exerts a similar effect to hydrochloric and nitric acids, but is less powerful. Sulphuric acid at low concentrations gives an effect resembling that of nitric and hydrochloric acids, but at higher concentrations the curve again begins to rise, and, in pure sulphuric acid, tartaric acid shows rotation values [α] red +69 and [α] violet +158·8, which are above those observed with any other solvent. With boric acid the rotatory dispersion curve of tartaric acid is unaffected in type, probably because of the formation of complex compounds of the two acids (compare Grossmann and Wieneke, A., 1906, ii, 209).

On adding increasing quantities of sodium hydroxide to the dextrorotatory aqueous solution of sodium tartrate, the rising rotatory-dispersion curve gradually flattens, and then, after becoming coincident with the horizontal axis corresponding with zero rotation, finally falls below on to the negative side of this axis; this alteration is attributed to the reversible formation of a lævorotatory tetrabasic salt of the acid. The addition of a calcium, strontium, magnesium, or cerium salt to the solution of tartaric acid containing excess of sodium hydroxide causes the curve for the alkaline solution to alter its character and to become wholly positive, doubtless due to the formation of complex compounds; a zinc salt gives no such evidence of complex formation.

Malic acid in the pure condition is dextrorotatory, but in the ionised condition exhibits a lævorotation; the addition of acids to the aqueous solution, as with tartaric acid, tends to repress dissociation, and the rotatory dispersion curve for the solution, which normally falls as it passes from red to violet, rapidly changes into a rising positive curve with the addition of increasing quantities of acid. Again, sulphuric acid at low concentration behaves like the other aqueous mineral acids, but in pure sulphuric acid malic acid attains the extreme negative values [α] red −27°, [α] violet −60·4°.

The effect of excessive sodium hydroxide on the activity of sodium malate solution resembles that with aqueous sodium tartrate; the rotatory dispersion curve becomes gradually flattened, and finally passes over to the other side of the horizontal axis representing zero-activity, the transition in this case being upwards from the negative side to the positive.

So-called anomalous rotatory dispersion as evidenced by maximum and minimum values or by achromatism occurs only in the neighbourhood of zero rotation, and the evidence indicates that it is due to the presence of two optically active components of different optical activity. Lowry's suggestion (A., 1914, ii, 786), to use the terms "simple" and "complex" rotatory dispersion in place of "normal" and "anomalous," is commended. D. F. T.

**The Relation of Position Isomerism to Optical Activity. XI. The Menthyl Alkyl Esters of Terephthalic Acid and its Nitro-derivatives.** JULIUS BEREND COHEN and HANNAH SMITH DE PENNINGTON (T., 1918, **113**, 57—66. Compare A., 1916, ii, 206).—The average molecular rotation of seven menthyl alkyl esters of terephthalic acid is found to be $[M]_D^{20}$ $-254°$, and the rotation of menthyl hydrogen terephthalate to be $[M]_D^{18}$ $-259·2°$, which may be compared with $-239°$ for menthyl benzoate, $-243°$ for menthyl alkyl phthalates, and $-332°$ for menthyl hydrogen phthalate. It appears, therefore, that the carbalkoxyl or carboxyl group has little influence, in the para-position, on the activity of the asymmetric carbon atom. In the case of some menthyl alkyl nitroterephthalates, it is likewise found that enhanced rotation is exhibited by those esters in which the nitro-group is adjacent to the active group. A strange abnormality is met with among these particular *o*-nitro-esters; the solutions in benzene have considerably higher rotations than the fused esters.

For details of the preparation and constants of these esters, see the original. J. C. W.

**Absorption of Hard Röntgen Rays in Gases.** MINNA LANG (*Ann. Physik*, 1917, [iv], **53**, 279—319).—The experiments described were made with highly penetrating rays, the absorptive powers of oxygen, nitrogen, air, carbon dioxide, hydrogen, sulphur dioxide, and methyl chloride being compared. The results obtained show the relative values of the absorption-coefficients for rays of varying penetrating power and the dependence of the absorptive power on the pressure of the gas. A comparison is made of the absorptive capacity of air for Röntgen rays and γ-rays. H. M. D.

**Interpretation of Röntgen Spectra.** L. VEGARD (*Ber. Deut. physikal. Ges.*, 1917, **19**, 328—343).—A theoretical paper, in which the author discusses the origin of the several series of lines which have been recognised in the high frequency spectra. It is assumed that the atoms are built up in accordance with Bohr's theory, and that the high frequency emission is to be explained on the lines adopted by this author.

According to Debye (A., 1917, ii, 434), the emission of the *K* series of lines is due to an inner ring of three electrons. This appears to be the most probable cause of the appearance of these lines, but it is shown that changes in a four-ring system of electrons may also account for the series.

The *L* and *M* series require the assumption of rings of electrons, the disturbance of which is associated with two or more energy quanta, and it is suggested that the origin of the *L* series is a seven-membered ring of electrons corresponding with two energy quanta, the *l* series an eight-membered ring with two quanta, and that the *M* series is due to a ring of nine electrons associated with three energy quanta. H. M. D.

**Atomic Structure on the Basis of Röntgen Spectra.** L. VEGARD (*Ber. Deut. physikal. Ges.*, 1917, **19**, 344—353).—The theoretical considerations advanced in explanation of the origin of the *K*, *L*, *l*, and *M* series of high frequency lines (compare previous abstract) have led the author to devise models for the structure of the known elements. It is claimed that this system of models is in agreement with the periodicity in the properties of the elements. With increasing atomic number there is a gradual increase in the number of concentric electron rings, but each ring appears to retain its individual characteristics throughout the entire series of elements. Such characteristics are the number of the constituent electrons and the energy quanta with which these are associated. The number of quanta increases, in general, with the diameter of the ring. H. M. D.

**Resonance and Ionisation Potentials for Electrons in Cadmium, Zinc, and Potassium Vapours.** JOHN T. TATE and PAUL D. FOOTE (*Proc. Nat. Acad. Sci.*, 1918, **4**, 9).—According to the observations of Franck and Hertz, there are certain definite potentials at which electrons cause the emission of rays by the atoms of a gas or vapour. Two types of collision occur, one of which is accompanied by the emission of a single frequency, whilst the other causes ionisation and gives rise to a composite spectrum. The corresponding potentials are distinguished as resonance and ionisation potentials, and these critical values of the potential have been determined for cadmium, zinc, and potassium vapours.

Within the limits of experimental error, the observed critical potentials agree with the values calculated from the quantum relation $h\nu = eV$, in which $\nu$ is the frequency of the single line in the case of the resonance radiation and the limiting frequency of the line series when the radiation is due to ionisation. H. M. D.

**Nomenclature of the Radio-elements.** ST. MEYER and E. VON SCHWEIDLER (*Zeitsch. Elektrochem.*, 1918, **24**, 36—38; *Physikal. Zeitsch.*, 1918, **19**, 30—32).—The authors, in a work published on radioactivity, have made a number of changes in the symbolic representation of radioactive substances. The changes, which have been assented to by twenty-nine German and Austrian chemists and physicists, consist chiefly in the following: (1) Isotopes are designated by Roman indices, for example, $U_I$, $U_{II}$. (2) Successive disintegration products are designated by Arabic indices, for example, $UX_1$, $UX_2$. (3) Branched products are designated by dashes, for example, Ra$C'$, Ra$C''$, the single dash indicating that the substances are like polonium and the double dash those like thallium.

J. F. S.

**The Colloidal State of Radioactive Substances.** HILARY ZACHS (*Kolloid Zeitsch.*, 1917, **21**, 165—176).—Many recorded observations show that certain radioactive substances in neutral or slightly alkaline solution exhibit properties which are usually regarded as characteristic of colloids, although the concentration of the solution is very much smaller than that corresponding with saturation with respect to the hydroxide. It has been suggested that the behaviour of these radioactive solutions is due to the presence of colloidal impurities in the solution, but certain facts cannot be reconciled with this hypothesis.

In the attempt to obtain further information on the subject, the author has investigated the properties of radium-*A*, radium-*B*, and radium-*C* in various solvents, including water, ethyl alcohol, ethyl ether, ethyl malonate, and benzene. The nature of the solvent is of considerable influence on the behaviour of the solutions in an electric field. In the case of water solutions, for instance, radium-*A* is deposited on the anode, radium-*B* on the cathode, and radium-*C* to a small extent on the anode, whereas in alcoholic solution, radium-*A* is deposited on the cathode and radium-*B* and -*C* on the anode. The sign of the change of the colloidal particles does not depend entirely on the nature of the solvent, for in every case, particles of opposite sign appear to be present. The results obtained with alcoholic solutions show, moreover, that the relative amounts of substance deposited on the two electrodes vary with the applied potential. This effect has been previously noted in the case of colloidal solutions of silver.

The adsorption of the radioactive colloids by various adsorbents is also found to exhibit a similar variation when the solvent is changed. The variability is said to afford evidence of the presence of particles of different degrees of dispersity, and it is suggested that the radioactive substances occur in the form of ions as well as in colloidal form.

Although cellulose has but little adsorptive capacity for the radioactive substances, it is found that comparatively large quantities of the radioactive products remain on the filter when the above solutions are passed through an ordinary filter paper. This would seem to show that a considerable proportion of the radioactive dispersoid particles are of large dimensions, and the suggestion is made that these particles contain a very large number of solvent molecules.

The decay of radium emanation in a gas or vapour leads apparently to the formation of gaseous ions by the combination of the particles of radium-*A*, -*B*, and -*C* with the molecules of the gas or vapour present. This type of combination or condensation seems to be very different in kind, however, from that which occurs in liquid solvents, in which, apparently, the degree of solvatation is such that colloidal properties are developed. H. M. D.

**Radioactive Minerals in Bavaria. II.** F. HENRICH (*J. pr. Chem.*, 1917, [ii], **96**, 73—85).—The view that the fluorspar (so-called "Stinkfluss") of Wölsenberg, near Wölsendorf, in the Upper Palatinate, owes its colour and odour to radioactive influences has been experimentally tested.

Crystallised colourless fluorspar can be coloured deep blue by the β- and γ-rays of radium, and then shows on gentle warming a beautiful green thermoluminescence, which fades and changes into the pale violet light characteristic of all fluorspars. But neither by radium nor by positive rays (Kanalstrahlen) could the characteristic odour of Wölsenberg fluorspar be produced. According to O. Ruff, this odour, which is produced when the mineral is crushed, is typical of free fluorine, and indeed the mineral may be used to demonstrate conveniently the odour of this difficultly prepared element.

The second part of the paper deals with the detailed analysis of copper–uranium mica (chalcolite or tobernite) from Steinbruch Fuchsbau, near Leopoldsdorf, in the Fichtelgebirge, the composition of which agreed closely with the formula

$$Cu(UO_2)_2(PO_4)_2,11{\cdot}5H_2O.$$

F. S.

**The Radioactivity of Archæan Rocks from the Mysore State, South India.** W. F. SMEETH and H. E. WATSON (*Phil. Mag.*, 1918, [vi], **35**, 206—214).—Some fifty radium estimations have been made of representative samples from the various components of the Archæan complex of Mysore, in order to see how far the various formations or groups are distinguishable by their radioactivity. These are set forth in order of age of the rock in a table. The oldest, the hornblende rocks (epidiorites and hornblende schists) of the Dharwar system, are low in radium and uniform, between 0·14 and 0·25 ($\times 10^{-12}$ gram of radium per gram of rock), and the rocks of the chloritic series, next in age, do not differ much from them. Intrusions of the Champion gneiss and the related quartz veins of the Kolar Field, which contain much more radium than the normal schists, considerably increase the radium content, whereas the basic intrusions of Dharwar age contain much less radium than the schists themselves. On radioactive evidence, the original classification which correlated the Bellara trap with the Grey trap of Chitaldrug is correct, rather than the newer correlation of the latter with the Santaveri trap of the Kadur district, which resembles it closely, but contains three times as much radium as the other two. This affords an example of the possible use of such determinations in the correlation of the highly metamorphosed members of the Archæan complex.

The Champion gneiss, Peninsular gneiss, and Closepet granite, next in age, contain four to five times as much radium as the Dharwar schists and twelve to fifteen times as much as the next and following Charnockites, which stand apart from the others in virtue of exceedingly low radium content. This confirms Holland's classification of Charnockites as a distinct petrographical province.

The general conclusions are that these very ancient rocks, all supposed to be of igneous origin, contain remarkably little radium. For the fairly uniform hornblendic schists of the Kolar Field, the radium content does not vary with the depth from the surface. Amongst magmas, the more basic contain less radium than the more acid, the Charnockite magma of intermediate composition being a striking exception. F. S.

**Influence of Heat Treatment on the Electrical and Thermal Resistivity and Thermo-electric Potential of some Steels.** EDWARD D. CAMPBELL and WILLIAM C. DOWD (*J. Iron Steel Inst.*, 1917, **96**, 251—266).—In a series of annealed and hardened steels containing from 0·018 to 1·184% of carbon, the ratio of the electrical resistivity to the relative thermal resistivity is in all cases higher than for pure iron. The effect of quenching is to raise both values. The thermo-electric potential varies with the nature as well as with the concentration of the elements dissolved in the iron. [See, further, *Ind.*, 1917, 1051.] C. H. D.

**A Permanganate Electric Cell.** A. W. WARRINGTON (*Chem. News*, 1918, **117**, 97—98).—Potassium permanganate is used as the depolarising agent in a two-fluid electric cell, in which the carbon plate is immersed in a dilute solution containing 3·16 grams of potassium permanganate and 6 c.c. of concentrated sulphuric acid in 250 c.c. of liquid, contained in a porous pot. The outer zinc compartment, of 750 c.c. capacity, contains a strong solution of zinc sulphate (14·55 grams). The cell gave a voltage of about 2. Two such cells were connected up to a water voltameter and tangent galvanometer in series, and, after the first ten minutes, the fall in current in a run extending over three hours forty-six minutes was from 0·09 to 0·085 ampere only, and the voltage at the end was still 3·7. With a single-fluid permanganate cell containing the same amounts of permanganate and sulphuric acid with amalgamated zinc and carbon, the current, after ten minutes, fell from 0·0538 to 0·0358 ampere in 146 minutes, whilst the voltage at the end was 1·5. The yield of current with very dilute solutions in a two-fluid cell is very high, and a cell containing 0·79 gram of potassium permanganate and 2·64 grams of sulphuric acid in 250 c.c. of liquid, and 3·59 grams of crystallised zinc sulphate in 750 c.c., deposited 0·48 gram of copper in three hours, whilst nearly 75% of the energy was still available. A similar dichromate cell, containing 5·88 grams of potassium dichromate and 13·72 grams of concentrated sulphuric acid in the carbon compartment, gave an average current of 0·0632 ampere only. B. N.

**The Magnetic Properties of Manganese and of some Manganese Steels.** Sir Robert Hadfield, C. Chéneveau, and Ch. Géneau (*Proc. Roy. Soc.*, 1917, [*A*], **94**, 65—87; *Compt. rend.*, 1918, **166**, 390—392).—Measurements have been made of the coefficient of magnetisation of manganese, free from occluded gases, and a number of manganese steels. Manganese is paramagnetic. [For numerical data, see *Ind.*, 12A.] W. G.

**Energy Theory of Matter.** Elmer B. Vliet (*Chem. News*, 1918, **117**, 118—119).—It has been pointed out by Thornton (A., 1917, ii, 164) that the molecular heat of combustion of an organic compound is proportional to the number of oxygen atoms which is required for the complete combustion of one molecule of the organic substance. According to Redgrove (A., 1917, ii, 411), the molecular heat of combustion can be represented by an additive series of terms which depend on the number and type of the valency bonds in the molecule.

By applying these relations to the aliphatic hydrocarbons, it is shown that the coefficients characteristic of the several terms in Redgrove's series may be calculated. The values so obtained differ from those calculated by Redgrove, and the conclusion is drawn that the molecular heat of combustion cannot be regarded primarily as a function of the number and type of the valency bonds. It is, however, still possible that the energy change accompanying a reaction may depend on the valency changes.

H. M. D.

**A High Temperature Thermostat.** J. L. Haughton and D. Hanson (*J. Inst. Metals*, 1917, **18**, 173—186).—The instrument consists in principle of a double-walled vessel, like a Bunsen ice calorimeter, made into a furnace by winding with nichrome wire. The vessel acts as a gas thermometer, and the variations of pressure of the air contained in it operate a contact-breaker, consisting of a U-tube containing mercury with two platinum contacts, through which passes a relatively small current. The latter, by means of a solenoid, pulls a fork out of or into two mercury cups, so introducing an external resistance into the heating circuit or cutting it out. The other side of the U-tube is connected with a second thermostat of simpler construction, which serves to compensate for changes of external pressure and temperature.

The furnace bulb is made of silica, and may be used for temperatures of the order of 1000°. The U-tube has a tap for removing the mercury when fouled by sparking, and is made sufficiently wide in the upper part of the limbs to prevent the mercury from being sucked back when the furnace is shut off. The cold thermostat consists of three concentric cylinders, of which the inner one acts as the air-bulb, and is surrounded by benzene contained in the middle vessel, on which a fine resistance wire is wound. The benzene, in expanding, operates a mercury contact-breaker. The third cylinder contains insulating material. With this arrangement, the temperature of this part of the apparatus is constant within less than 0·1°. The main furnace is then kept constant within 1°.

By connecting another furnace, such as a crucible furnace, in series with the main regulating resistance, but in parallel with a thermostat furnace, the temperature of the former may be kept constant with about the same accuracy as the thermostat. By automatically reducing a resistance in parallel with the controlled furnace, very regular cooling may be obtained, such as is required in taking cooling curves. C. H. D.

**Adsorption Compounds and Adsorption. III. The Influence of the Adsorption of certain Substances by Alcohol.** L. Berczeller and St. Hetényi (*Biochem. Zeitsch.*, 1917, **84**, 137—148).—A number of measurements are given of the adsorption of alkali hydroxides, acetic acid, iodine, methylene-blue, etc., by starch, charcoal, etc., and the influence of the additions of alcohols. The influences of isocapillary and equimolecular solutions of the alcohols on adsorption were compared. Generally, the isocapillary solutions did not exert the same amount of inhibition, the solutions of lower alcohols, which contain a relatively large amount of alcohol, exerting a greater inhibition than isocapillary solutions of the higher alcohols. Those isomolecular solutions of which the surface tensions are lowest exert, however, a greater inhibitory action. S. B. S.

**Gliding Dialysis. II.** H. Thoms (*Ber.*, 1918, **51**, 42—45. Compare A., 1917, ii, 561).—Instead of rotating the dialyser about the plane of the membrane, it may be rotated or shaken in the same plane, with equally good results. The new arrangement is an improvement, inasmuch as it imposes very little tearing strain on the membrane. [See, further, *Ind.*, 190A.] J. C. W.

**Solubility and Dissociation of some Electrolytes in Ethylurethane.** M. Stuckgold (*J. Chim. Phys.*, 1917, **15**, 502—516).—The author has determined the solubilities of the following salts in ethylurethane at 60°: ammonium, rubidium, potassium, tetramethylammonium and tetraethylammonium iodides, sodium, potassium, rubidium, and tetramethylammonium bromides, sodium, potassium, and ammonium chlorides. The conductivities of six electrolytes, namely, ammonium, potassium, and tetraethylammonium iodides, tetramethylammonium bromide, cobalt nitrate, and zinc nitrate, have been determined, those of the iodides being taken to the greatest dilutions suitable, considering experimental errors. The cryoscopic constant of this solvent, using naphthalene, carbamide, and nitrotoluene as solutes, was found to be 53·2, and from this, molecular weight determinations by the cryoscopic method indicated that ammonium, potassium, and rubidium iodides are dissociated in ethyl urethane.

Molecular weight determinations on ethylurethane, based on the capillarity constant, using the formula $M = 0{\cdot}6T(4{\cdot}8 - \log p)/a_2$, where $T$ is the absolute b. p. at $p$ mm. of mercury and $a_2 = h \, . \, r$, where $h$ is the height of ascension and $r$ the radius of the capillary in millimetres, show that ethylurethane is strongly polymerised, the factor of association being almost independent of the temperature over the range 65—179°. The viscosities and densities of the urethane at 60°, 70°, and 80° were also determined. W. G.

**Ultrafiltration of Supersaturated Solutions.** L. Berczeller (*Biochem. Zeitsch.*, 1917, **84**, 156—159).—Supersaturated solutions of menthol, thymol, and naphthol were filtered through collodion membranes, and the surface tensions of filtrate and residue were determined by the stalagmometer. In certain cases, the results (lower surface tension of residue) indicated that some of the solute was retained on the filter, from which fact the conclusion is drawn that the supersaturated solution is colloidal in character.

S. B. S.

**Colloidal Nature of the γ-Alkali Resin Soaps.** Ludwig Paul (*Kolloid Zeitsch.*, 1917, **21**, 176—191).—A general account is given of the properties of solutions of sodium and ammonia resin soaps in which particular attention is directed to the colloidal properties of the solutions and to differences between the resin and fatty acid soaps. Dilute solutions of the alkali resin soaps represent highly disperse colloid systems of very pronounced stability. On the addition of basic dyes, such as methyl-violet and magenta, colloidal lakes are formed which can be kept without change for prolonged periods of time. The lakes are coagulated on the addition of suitable electrolytes.

On addition of hydrochloric acid to the γ-alkali resin soaps, γ-pinic acid is obtained, and this behaves very similarly to the soaps towards basic dyes. [See *Ind.*, April.] H. M. D.

**Colour and Degree of Dispersity [of Colloidal Solutions].** L. Berczeller (*Biochem. Zeitsch.*, 1917, **84**, 156—174).—Gold sols have varying colours, according to the size of the colloidal particles, and Harrison (A., 1912, ii, 240) has directed attention to the similarity of the colours of the adsorption complexes of iodine with starch and dextrins, where similar variations of colour are produced by varying the size of the particles of the carbohydrate. The author shows that similar variations in the colour of the adsorption complexes of lanthanum hydroxide can be produced by varying the size of the particles of the hydroxide. Attention is also directed to analogies in the colour variations in certain complex copper compounds, in certain reactions of bile pigments, in some furfuraldehyde reactions (Udránszky, A., 1889, 1024; 1891, 350), and in the nuances of solutions of dyes when subjected to varying treatments (heating, dilution, treatment with salts, etc.).

S. B. S.

**Anisotropic Colloidal Solutions.** W. REINDERS (*Kolloid Zeitsch.*, 1917, **21**, 161—165. Compare Diesselhorst and Freundlich, A., 1916, ii, 65; Kruyt, *ibid.*, ii, 486).—With a view to the explanation of the double refraction which is exhibited by certain colloidal solutions, further experiments have been made with vanadium pentoxide sols which seem to show that the particles of such sols are crystalline. By varying the conditions of formation of the pentoxide, it has been found that there is no clear line of demarcation between the particles which are present in the initially isotropic sols and those which can be microscopically identified as crystalline particles. Although the double refracting power of a sol is only developed very slowly at the ordinary temperature, the transformation takes place much more quickly at 100°. In the freshly prepared sols, the ultra-microns are spherical, but on heating at 100°, elongated ultra-microns make their appearance in a short time. These increase in size and number, and the change is accompanied by a considerable increase in the viscosity.

Experiments made with mercurous chloride and lead iodide gave similar results. If these substances are prepared by double decomposition in presence of a protective colloid, doubly refracting sols are obtained, but there is a continuous transition from the sol condition to that which is represented by crystalline suspensions of these substances.

The anisotropic character of the sols in question appears therefore to be due to the crystalline nature of the ultra-microns.

H. M. D.

**Kinetics of the Reactions in the Formation and Flocculation of Colloidal Solutions.** L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 175—182).—Iodic acid accelerates the reduction of gold chloride solutions by sulphurous acid, as do also mercuric salts, and the colour of the sols varies in the latter case with the salt used. Examples are given of the influence of capillary active substances (hexoic and decoic acids) on the flocculation of colloidal gold and starch solutions, which are cases of sensitisation of colloids to salt precipitation, as recently demonstrated by Freundlich and Rona (A., 1917, ii, 365). S. B. S.

**Coagulation and the Attraction of Particles.** RICHARD ZSIGMONDY (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 1—43; from *Chem. Zentr.*, 1917, ii, 350—351 *).—The paper deals with the possibility of determining the attraction (if any) between discharged colloidal particles from measurements of the rate of coagulation. Experiments in which the changes of colour of gold hydrosols were employed as an indicator of the progress of the coagulation showed that a pure colloidal gold solution of a given nature and concentration has a certain minimum time of coagulation, independent of the nature, and to a great extent independent of the concentration, of the electrolyte employed. The period of rapid coagulation is reached before the particles are completely discharged, but the remaining charges are small (compare Hardy and Powis, *Zeitsch. physikal. Chem.*, 1915, **89**, 179). The time of coagulation is approximately proportional to the gold concentration. A method of observing the progress of coagulation ultramicroscopically is given, and by this means the diminution in the number of primary particles and the production of secondary particles (which shine more brightly) were determined. From these results, it is calculated that the sphere of attraction of a primary particle is two or three times its radius. This is in agreement with the results obtained by other writers in other ways. It is proved, therefore, that the discharged particles do attract one another when they come within this distance of each other. R. V. S.

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* and *Zeitsch. physikal. Chem.*, 1918, **92**, 600—639.

**Retardation of the Formation of Prussian Blue and other Reactions in Aluminium Hydroxide Sols.** JOSEF REITSTÖTTER (*Kolloid Zeitsch.*, 1917, **21**, 197—200).—In the course of observations on the coagulation of aluminium hydroxide sols in presence of various alkali metal salts (Gann, A., 1916, ii, 382), it was found that after coagulation by the addition of a very dilute solution of potassium ferrocyanide, the solution gave no blue coloration on the addition of ferric ions until after the lapse of a considerable interval of time. To explain this effect, it was suggested that the ferrocyanide ions are adsorbed and subsequently enveloped by the coagulate.

Further experiments show that the retardation is very much less pronounced if some other coagulating electrolyte, such as sodium citrate, is added to the sol either before or after the addition of the ferrocyanide. In these circumstances, it is more probable that the retardation of the formation of Prussian blue is to be explained by the adsorption of both the ferrocyanide and the ferric ions. If either or both are then displaced by other ions, conditions favourable to the formation of Prussian blue are obtained.

Similar retardation phenomena have been found when a little of the blue sol obtained by acidifying Congo-red is mixed with a colloidal solution of aluminium hydroxide and a drop of sodium hydrogen carbonate solution is added to the mixture. The blue sol may be replaced by benzopurpurin or rosolic acid. [See *Ind.*, 71A.] H. M. D.

**General Curves for the Velocity of Complete Homogeneous Reactions between Two Substances at Constant Volume.** GEORGE W. TODD (*Phil. Mag.*, 1918, [vi], **35**, 281—286).—By choosing suitable quantities to represent the concentration of the reacting substances, it is possible to plot curves showing the connexion between the rate of change and the time, which are applicable to all reactions of the same type. The mode of representation may be illustrated by reference to the bimolecular velocity equation $dx/dt=k(a-x)(b-x)$. If $X=x/a$, $K=ka$, and $p=b/a$, this equation assumes the form $dX/dt=K(1-X)(p-X)$, and on integration this gives $Kt=1/(1-p).\{\log p(1-X)/(p-X)\}$. The curves referred to are then obtained by plotting $X$ against $Kt$ for values of $p=1{\cdot}5$, 2, 3, etc.

Corresponding series of curves are plotted for the termolecular reaction represented by $2A + B \longrightarrow$ for the three cases in which the initial concentration of $A$ is equal to, greater, and less than that of $B$. Curves for the quadrimolecular reaction $3A + B \longrightarrow$ and $2A + 2B \longrightarrow$ are also shown.

These general curves may be applied in practice for the determination of $k$, of the value of $X$ corresponding with a given time interval, or for the determination of the order of a reaction. If the order of the reaction and the initial concentration are known, it is only necessary to measure $X$ corresponding with a certain value of $t$, and the curves then give $Kt$, and therefore $k$. The fraction $X$ changed in a given time may be read off from the curves if the order of the reaction, the coefficient $k$, and the initial concentrations are known. To find the order of a reaction, it is necessary to know the initial concentrations and two corresponding values of $X$ and $t$. The particular curve on which the two points ($X$, $t$) fit most exactly determines the order of the reaction.

H. M. D.

**Relationship between the Saponification Velocity Constants of Esters.** P. E. Verkade (*Chem. Weekblad.*, 1918, **15**, 203—208).—The author finds that the ratio of the velocities of saponification of mixed anhydrides of acetic, propionic, etc., acids with different acids is always the same.

A. J. W.

**Velocity of Saponification of certain Esters by Tenth-normal Potassium Hydroxide in Different Solvents at 25°.** Ernest Anderson and H. B. Pierce (*J. Physical Chem.*, 1918, **22**, 44—67).—The object of these experiments was to determine whether the relative velocities of saponification of different esters are affected by the nature of the solvent and whether the relative rates of saponification of different esters containing the same alcohol (or acid) are independent of the nature of the alcohol (or acid).

The rates of saponification of twenty-three esters were measured at 25° in 90% methyl alcohol, 90% ethyl alcohol, *iso*amyl alcohol, $D^{20}_{15}$ 0·8166, and, when possible, in water. The results obtained show that the relative values of the velocity coefficients in the different solvents vary considerably with the nature of the ester. Esters containing the same alcohol (acid) are saponified at relative rates which depend on the nature of the alcohol (acid).

H. M. D.

**Hydrolysis of Triethyl Citrate and the Ethyl Hydrogen Citrates.** Joh. Pinnow (*Zeitsch. Elektrochem.*, 1918, **24**, 21—36).—The hydrolysis of triethyl citrate, symmetrical and unsymmetrical diethyl hydrogen citrate, and symmetrical and unsymmetrical ethyl dihydrogen citrate by means of sodium hydroxide has been studied at a series of temperatures from 0° to 100°. The hydrolysis of the various stages is shown to take place at very different velocities between the temperatures of 8° and 50°. Each step in the hydrolysis may be separated from the others, and goes to completion as a strictly bimolecular reaction. The side ethyl groups are the first to be removed, and in no circumstances do symmetrical diethyl hydrogen citrate or unsymmetrical ethyl dihydrogen citrate appear in recognisable quantities as products of any of the hydrolyses. These products are only obtainable by the esterification of citric acid. The preparative separation of the mono- and di-ethyl esters from one another and from citric acid can be effected by ether extraction from aqueous solution in a Partheil-Rose apparatus. The various esters were identified by measurements of their hydrogen ion concentration by means of the colorimetric process of Friedenthal, Salesky, and Salm. The temperature coefficient of the rate of hydrolysis is high for all five compounds at temperatures below 23°; in the case of the unsymmetrical diethyl ester and the monoethyl esters a minimum is shown between 23° and 30°, and a second minimum for the monoethyl esters between 45° and 60° and 38° and 45° respectively. The stepwise hydrolysis and the first minimum of the temperature coefficient are explained by the formation of additive products between the ester and the alkali, these compounds undergoing decomposition as the hydrolysis proceeds into the original compounds. The following reaction constants and temperature coefficients have been found: Hydrolysis of triethyl citrate, $k=37\cdot8$ at 8·1°, 63·7 at 15°, 98·9 at 23°, 149·8 at 30°, 253 at 40°, and 443 at 50°; increase of $\log k$ for 10° between the successive temperatures is 0·328, 0·239, 0·259, 0·227, and 0·243. Unsymmetrical diethyl hydrogen citrate, $k=1\cdot725$ at 8·1°, 2·92 at 15°, 4·28 at 23°, 5·14 at 30°, 9·38 at 40°, 16·17 at 49°; increase of $\log k$, 0·330, 0·208, 0·114, 0·262, and 0·263. Symmetrical diethyl hydrogen citrate, $k=0\cdot474$ at 6·7°, 0·841 at 15°, 1·48 at 23°, 2·27 at 30°, 4·16 at 40°, and 6·84 at 50°; increase of $\log k$, 0·300, 0·306, 0·266, 0·263, and 0·216. Symmetrical monoethyl hydrogen citrate, $k=0\cdot0038$ at 0°, 0·0149 at 15°, 0·0283 at 23°, 0·0409 at 30°, 0·0743 at 38°, 0·1153 at 45°, 0·245 at 60°, 0·584 at 75°, and 2·86 at 100°; increase of $\log k$, 0·395, 0·349, 0·229, 0·324, 0·273, 0·218, 0·251, and 0·276. Unsymmetrical monoethyl hydrogen citrate, $k=0\cdot0825$ at 8°, 0·132 at 15°, 0·238 at 23°, 0·302 at 30°, 0·511 at 38°, 0·654 at 45°, 0·080 at 55°, 1·76 at 65°, and 10·65 at 100°; increase of $\log k$, 0·291, 0·320, 0·147, 0·285, 0·154, 0·217, 0·213, and 0·212. The figures in all cases refer to the hydrolysis of a single ethyl group.

J. F. S.

**Rate of Solution of Silver in Chromic Acid.** R. G. VAN NAME and D. U. HILL (*Amer. J. Sci.*, 1918, [iv], **45**, 54—58).—The measurement of the rate at which silver dissolves in chromic acid solutions containing sulphuric acid has shown that the initial velocity is greater than the velocity which characterises the normal dissolution process. The anomaly indicates that the velocity depends on the physical state of the metal, and this in turn suggests that the rate of dissolution of the metal is not entirely determined by diffusion process.

Previous experiments have shown that the rates of dissolution of different metals tend to become more nearly equal as the concentration of the sulphuric acid in the solution increases. The behaviour of cadmium and silver forms an exception to this rule, in that the relative rates of dissolution diverge with increasing acid concentration. H. M. D.

**Contact Catalysis. IV.** WILDER D. BANCROFT (*J. Physical Chem.*, 1918, **22**, 22—43. Compare this vol., ii, 40).—A discussion of false equilibria in reference to the poisoning of catalysts by the adsorption of one or other of the products of reaction. Such adsorption will cause the reaction to slow down, and it may be brought practically to a standstill. In these circumstances, an apparent or false equilibrium is reached which will depend on the relative amount of the catalyst present. It is probable that molten sulphur catalyses the reaction between hydrogen and sulphur, and that hydrogen sulphide acts as a poison towards the catalyst. A similar effect is supposed to obtain in the reaction between hydrogen and selenium.

Enzyme reactions are in many cases affected by the products of reaction, in that a large quantity of enzyme is required to complete the reaction. In such cases, false equilibria are set up which may be explained in terms of the poisoning of the enzyme by one or other of the reaction products. H. M. D.

**The Variations in the International Tables of Atomic Weights.** TH. RENARD (*J. Chim. phys.*, 1917, **15**, 541—548).—A brief discussion of the revisions made of the various atomic weights by the International Committee since 1903. The author advocates the use of the rounded-off values suggested by Guye (compare A., 1916, ii, 386). W. G.

**Hydrogen Isotopy.** A. E. LACOMBLÉ (*Chem. Weekblad*, 1918, **15**, 38—40).—Polemical. A criticism of the views expressed by Scheringa (*ibid.*, 1917, **14**, 953) on the relationship of Prout's hypothesis to the periodic system. A. J. W.

**Prout's Hypothesis and the Periodic System.** K. SCHERINGA (*Chem. Weekblad*, 1918, **15**, 221).—A reply to Lacomblé (preceding abstract). A. J. W.

**The Exchange of Energy in the Collisions between Slowly-moving Electrons and Molecules of Gases.** G. HERTZ (*Ber. Deut. physikal. Ges.*, 1917, **19**, 268—288).—A theoretical paper in which the laws governing the exchange of energy between colliding electrons and molecules are discussed in reference to atomic and molecular structure. From the available data for helium, it is calculated that the loss of energy in the collision between an electron and a helium atom is 0·00027 times the energy of the electron. This result is very nearly the same as that which is derived on the assumption that the laws of collision are those governing collisions between elastic spheres, and from the close agreement the conclusion is drawn that the energy lost by the electron is represented by the increase in the kinetic energy of the helium atom. In the case of hydrogen, however, the loss of energy is found to be much greater, namely, 0·06 of the energy of the electron, and it would seem that the collision of an electron with a hydrogen molecule is accompanied by an increase in the internal energy of the molecule.

The movement of electrons in gases at higher pressures and the influence of small quantities of impurities on the effects produced are also discussed from the point of view of the author's theory.

H. M. D.

**Valency Centres. III. The Periodic System.** O. HINSBERG (*J. pr. Chem.*, 1917, [ii], **96**, 166—173. Compare A., 1916, i, 725; 1917, ii, 173, 461).—As explained in the earlier papers, the atoms of the elements lithium, glucinum, boron, and carbon are assumed to possess one valency centre, the chemical valency of which ranges from one to four, the maximum being attained at carbon; in the remaining elements of the first group, the atoms contain two valency centres, one being quadrivalent throughout and the other gradually increasing in valency from 1 to 4, so that the surplus or normal valency falls in the order 3, 2, 1, 0 for nitrogen, oxygen, fluorine, and neon respectively. Similar differences exist in the second series of the periodic system; a single valency centre or atomic nucleus is present in the first four members, but at the fifth element, namely, phosphorus, a second valency centre enters, and the remainder of the elements of the series up to argon contain the two atomic nuclei which in the last element just satisfy one another and leave the element without free valency; contrary to the earlier opinion, chlorine probably contains only two valency centres, this view receiving support from the similarity in the general properties of the chlorides and cyanides, and the analogy between the intra-atomic structure of the chlorides and the intramolecular structure of the cyanides, for example, $\underset{\smile}{\overset{\frown}{\cdot{-}\cdot}}{-}\mathrm{Ag}$ for silver chloride and $\underset{\smile}{\overset{\frown}{\mathrm{N{-}C}}}{-}\mathrm{Ag}$ for silver cyanide. In the next series, a different type is encountered; the assumption is made that in these elements a sexavalent atomic nucleus is present, in which the active valency increases by units from potassium up to the maximum of six, which is attained at chromium; the atoms of the succeeding elements, manganese, iron, cobalt, and nickel, include an additional valency centre which possesses an additional free valency at each element named, so that the maximum possible valency for these metals is 7, 8, 9, and 10 respectively, the maximum apparently being attained in iron carbonyl, $Fe(CO)_4$, with octavalent iron; in the case of cobalt, the full possible nonavalency is never reached, the differential valency, or the difference between the valency of the sexavalent and tervalent nuclei supplying the maximum; with nickel also the differential valency has a value 2, in agreement with the composition of most of the compounds, although in nickel carbonyl, $Ni(CO)_4$, the atom appears to attain octavalency, but, however, is still short of decavalency. The metallic nature of the whole of the ten elements of this third series is ascribed to the presence of the sexavalent atomic nucleus. Copper is regarded as a transition element between the third and fourth series, and therefore probably abnormal; from zinc onwards, the members of the fourth series fall into a normal group, the valency of the first atomic nucleus gradually increasing in valency until quadrivalent germanium is reached; after this point, the atoms of this series contain a second atomic nucleus the valency of which gradually increases from unit value in arsenic to 4 in krypton, the latter therefore being devoid of free valency. For the present, the theory is extended only as far as the fifth and sixth groups; the elements of the former contain as their essential characteristic a sevavalent atomic nucleus which exerts its full effect in molybdenum, the last four elements of the group (one unknown) including an additional nucleus, but the final elements, namely, rhodium and palladium, exert only their differential valency. Silver, like copper, is probably an abnormal transition element. The sixth series, from cadmium to xenon, is normal, and corresponds with the zinc–krypton group. D. F. T.

# Inorganic Chemistry.

**The Hydrides of the Metalloids.** R. DE FORCRAND (*J. Chim. phys.*, 1917, **15**, 517—540).—An elaboration of work already published (compare A., 1905, ii, 696) and a discussion of Berthoud's work on this subject (compare A., 1917, ii, 237). W. G.

**Hydrogen Peroxide as a Reducing Agent.** M. KLEINSTÜCK (*Ber.*, 1918, **51**, 108—111).—Silver chloride, suspended in potassium hydroxide solution, is quickly reduced by hydrogen peroxide according to the equation $2AgCl + H_2O_2 + 2KOH = 2Ag + O_2 + 2KCl + H_2O$.

Carbonyl chloride and phenyl carbonate also react with alkaline hydrogen peroxide, and so does a saturated solution of potassium hydrogen carbonate if kept at 100° in a pressure bottle. The distillate obtained by passing steam through the products reduces ammoniacal silver oxide, and is therefore said to contain formaldehyde. The author sees in these reactions a new interpretation of the assimilation of carbon dioxide by plants, thus: $H_2CO_3 + H_2O_2 = CH_2O + H_2O + 3O$. [See also *Ind.*, April.] J. C. W.

**Variations of the Density of Air and the Loomis-Morley Law.** PH. A. GUYE (*J. Chim. phys.*, 1917, **15**, 561—566).—A study of the results obtained by various workers for the weight of a normal litre of air, in which it is shown that the results, taken as a whole, verify the qualitative experimental relation, stated by Loomis and Morley, between the density of the air and the barometric pressure. The most probable explanation of such variations in density is based on the presence in the air of varying quantities of dust, invisible under the ultramicroscope. The mean of the most modern determinations gives the value 1·2928 grams as the weight of a normal litre of air. W. G.

**Portable Hydrogen Sulphide Generator.** W. Faitoute Munn (*J. Ind. Eng. Chem.*, 1918, **10**, 130—131).—A wide glass tube has two bulbs formed at its lower end, the bottom bulb being provided with a draw-off tap. A perforated lead plate is fitted at the constriction between the bulbs (a piece of glass tubing in the lower bulb acts as a support for the plate) and ferrous sulphide is filled into the upper bulb. The acid reservoir consists of a large bulb, the stem of which passes through a cork closing the top of the wide glass tube and extends to the bottom of the lower bulb. A tapped exit tube for the gas is placed near the top of the wide tube, and this exit tube is fitted with a small washing tube. W. P. S.

**Automatic Hydrogen Sulphide Stopcock.** Carl H. Classen (*J. Ind. Eng. Chem.*, 1918, **10**, 131—132).—To the delivery tube of the hydrogen sulphide apparatus is attached a length of rubber tubing in which is inserted a glass "pearl" made from glass tubing having a diameter slightly larger than that of the rubber tubing. When the rubber tubing over the "pearl" is compressed between the finger and thumb, a channel for the flow of the gas is formed between the glass and the rubber. W. P. S.

**Chloro- and Bromo-aminosulphonic Acids.** Wilhelm Traube and E. von Drathen (*Ber.*, 1918, **51**, 111—115).—Solutions of potassium aminosulphonate and hypochlorous acid in equivalent proportions react in the cold to form *potassium chloroaminosulphonate*, $NHCl{\cdot}SO_3K$, which may be isolated by evaporating the mixture to a small bulk, in a high vacuum, at as low a temperature as possible and precipitating with alcohol. The salt forms limpid, hygroscopic crystals, and is comparatively stable. When warmed with mineral acids, hydrolysis takes place according to the equation $NHCl{\cdot}SO_3H + H_2O = NH_2Cl + H_2SO_4$. The corresponding *barium* salt is not so stable, but *potassium bromoaminosulphonate* is very similar.

Similar salts may be prepared by the interaction of free aminosulphonic acid and metallic hypochlorites. Alkylaminosulphonates apparently give very unstable products, for evolution of gas is noticed as soon as hypochlorous acid is added.

There are indications that a double amount of hypochlorous acid produces less stable dichloroaminosulphonates. J. C. W.

**Rate of Hydrolysis and Electrical Conductivity of Hypophosphoric Acid Solutions.** R. G. Van Name and Wilbert J. Huff (*Amer. J. Sci.*, 1918, [iv], **45**, 103—118).—The iodometric method for the estimation of phosphorous acid in presence of hypophosphoric acid (this vol., ii, 128) has enabled the authors to investigate the rate of hydrolysis of the latter acid. The data obtained at 25° and 60° show that in dilute solutions containing hydrochloric acid as catalyst the hydrolysis proceeds in accordance with the equation for a unimolecular change. The velocity coefficient increases much more rapidly than the hydrogen ion concentration. The temperature coefficient for 10° is 2·7. The fact that the hydrolysis follows a unimolecular law is in favour of the formula $H_4P_2O_6$ rather than $H_2PO_3$ for hypophosphoric acid, for the production of phosphorous and phosphoric acids would require the interaction of two molecules of acid if it had the simpler formula.

For the conductivity measurements, pure solutions of the acid were prepared from lead and copper hypophosphate by the action of hydrogen sulphide at low temperatures. The metallic sulphides were filtered off and the excess of hydrogen sulphide removed by a current of air. The conductivity of the solutions after complete hydrolysis was also determined.

The molecular conductivity at 25° referred to the formula $H_4P_2O_6$ increases from $\Lambda = 384{\cdot}7$ at $v = 32$ to $\Lambda = 629{\cdot}3$ at $v = 1024$. After hydrolysis, the conductivity of the stronger solutions is diminished, whilst that of the more dilute solutions is increased.

Attention is directed to the resemblance between the properties of hypophosphoric acid and pyrophosphoric acid. This resemblance is found in the conductivity of the solutions, in the behaviour towards indicators, and in their solubility relations, and may be adduced in support of the formula $H_4P_2O_6$ for hypophosphoric acid. H. M. D.

**Preparation of Amorphous Boron.** WILHELM KROLL (*Zeitsch. anorg. Chem.*, 1918, **102**, 1—33).—The paper gives the results of numerous experiments on the reduction of boron compounds. Aluminium is unsuitable. Sodium yields mixtures of the lower oxides of boron mixed with boride. Calcium produces only borides. Magnesium may be used for the reduction of boric acid, but the product contains more than 3% Mg in the form of insoluble boride. The halogen compounds of boron can be reduced by potassium, sodium, magnesium, and aluminium; in each case, borides of the metal are formed as well as free boron. The purest boron is obtained by the reduction of boron chloride with hydrogen in the high tension electric arc. Red phosphorus does not reduce boric acid.

When boric acid is heated with magnesium nitride, a *boron nitride*, probably $B_3N$, is produced. Boron nitride, BN, can be conveniently prepared from boric acid and calcium cyanamide.

When boron chloride is passed over red phosphorus in the presence of oxygen, a *phosphate*, $2B_2O,P_2O_5$, is formed. Other phosphates appear to exist.

The original contains details as to analytical processes regarding compounds of boron. [See, further, *Ind.*, 148A.] R. V. S.

**Nomenclature of Silicon Compounds.** ALFRED STOCK (*Ber.*, 1917, **50**, 1769—1771. Compare A., 1917, ii, 204).—The author again emphasises the fact that very little chemical similarity exists between silicon and carbon compounds of the same structure, and proposes to abandon the nomenclature of carbon chemistry as far as possible. For example, the radicle $-SiO \cdot OH$ in no way resembles a carboxyl group, and therefore the term "hydroxyoxo" is suggested in such a case. J. C. W.

**Silicon Hydrides. II. Bromination of Monosilane, $SiH_4$. $SiH_3Br$ and $SiH_2Br_2$.** ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1917, **50**, 1739—1754. Compare A., 1916, ii, 319).—The experiments, fully described in this paper, had for their object the bromination of pure silane under conditions favourable to the production of the lower bromides. Under ordinary conditions, the reaction between bromine and silane is very violent, but if an excess of the gas is led into a large vessel on the walls of which solid bromine is deposited, and the temperature is maintained at about −80° to −70°, the mono- and di-substitution products can be obtained comparatively free from $SiHBr_3$ and $SiBr_4$.

The apparatus employed is very elaborate (see A., 1917, ii, 442) and the manipulation is a matter of considerable difficulty. For details of the preparations and final fractionations, the original should be consulted.

*Bromomonosilane*, $SiH_3Br$, is a colourless gas with a pungent odour, at the same time reminiscent of monosilane. It has m. p. −94°, b. p. +1·9°/760 mm., $D^0$ 1·533, and molecular latent heat of vaporisation 5·83 Cal. It may be preserved over mercury for some time, but it detonates on exposure to the air, giving silicic acid and brown silicon. It reacts with cold water according to the equation $2SiH_3Br + H_2O = 2HBr + (SiH_3)_2O$ (see following abstract), whilst it may be analysed by measuring the volume of hydrogen produced under treatment with 30% sodium hydroxide, according to the equation $SiH_3Br + 3NaOH = 3H_2 + NaBr + Na_2SiO_3$.

*Dibromomonosilane*, $SiH_2Br_2$, is a colourless, mobile, highly refractive liquid, m. p. −70·1°, b. p. 66°/760 mm. (extrapolation; highest recorded value, 18°/123 mm.), $D^0$ 2·17, molecular latent heat of vaporisation 7·41 Cal. In carefully dried vessels, it may be kept for a long time, but it inflames in the air. It is very sensitive to moisture, being decomposed into hydrogen bromide and a solid, $(SiH_2O)_x$. Alkalis decompose it according to the equation $SiH_2Br_2 + 4NaOH = 2H_2 + 2NaBr + Na_2SiO_3 + H_2O$.
J. C. W.

**Silicon Hydrides. III. Disiloxane, $(SiH_3)_2O$; Tetrachloromonosilane, $SiCl_4$; Hexachlorodisiloxane, $(SiCl_3)_2O$.** ALFRED STOCK, CARL SOMIESKI, and ROBERT WINTGEN (*Ber.*, 1917, **50**, 1754—1764).—When bromomonosilane is shaken with water, it changes into *disiloxane*, $(SiH_3)_2O$, the preparation and purification of which are now described. It is a colourless, odourless gas which does not inflame spontaneously, but burns with a brilliant light, giving a white smoke and a deposit of brown silicon. It has m. p. −144°, b. p. −15·2°, $D^{-80}$ 0·881, molecular latent heat of vaporisation 5·63 Cal. (compare $SiH_4$, 3·03; $Si_2H_6$, 5·18; $Si_3H_8$, 7·13; $Si_4H_{10}$, 9·18 Cal.). The m. p. and b. p. are lower than the constants for the parent hydride, $Si_2H_6$ (m. p. −132·5°, b. p. −15°), which is the reverse of the relationships between ethane and dimethyl ether. It only decomposes rapidly under the influence of heat when raised to redness. Submitted to a discharge of electric sparks, it slowly yields pure hydrogen. When mixed with oxygen, it inflames or explodes at once, the alteration in volume being in accordance with the equation $(SiH_3)_2O + 3O_2 = 2SiO_2 + 3H_2O$. It is not appreciably soluble in water, but soon decomposes into hydrogen and insoluble products, like $(SiH_2O)_x$, etc. With sodium hydroxide, however, decomposition is complete, according to the equation $(SiH_3)_2O + H_2O + 4NaOH = 2Na_2SiO_3 + 6H_2$, which may be applied in the analysis of the gas.

Disiloxane and chlorine react very vigorously at −125°; the primary product, hexachlorodisiloxane, may be isolated, but most of it decomposes according to the equation $4(SiCl_3)_2O = 2SiO_2 + 6SiCl_4$, and some brown silicon is even formed as well. "*Tetrachloromonosilane*" (silicon tetrachloride) has m. p. −68·7°, b. p. 56·8°/760 mm., molecular latent heat of vaporisation 7·19 Cal., and "*hexachlorodisiloxane*" is now found to have m. p. −33° and b. p. 137°/760 mm.

It is an interesting fact that disiloxane is the first volatile compound of silicon, hydrogen, and oxygen. Many derivatives, with the same elements, are known, such as "silicoformic anhydride," $(O{:}SiH)_2O$, but these must assuredly be polymerides, whereas alkyl, alkoxyl, and similar derivatives of the true monomeric type, for example, $(SiR_3)_2O$ and $[Si(OR)_3]_2O$, have frequently been prepared (compare Martin and Kipping).

Apparently, the compound $SiH_3{\cdot}OH$, which would be the primary product of the action of water on $SiH_3Br$, is very unstable. It is noteworthy that the alkyl derivatives, $SiR_3{\cdot}OH$, also change into oxides readily, but the alkyl groups do confer a measure of stability on them, for hexaphenyldisiloxane, $(SiPh_3)_2O$, changes back into $SiPh_3{\cdot}OH$ on boiling with alcoholic potassium hydroxide (Kipping and Lloyd, T., 1901, **79**, 455). J. C. W.

**Silicon Hydrides. IV. Oxomonosilane (Protosiloxane).** Alfred Stock, Carl Somieski, and Robert Wintgen (*Ber.*, 1917, **50**, 1764—1769).—Dibromomonosiloxane reacts with water to form hydrogen bromide and a volatile compound, which is very probably *oxomonosilane* (*protosiloxane*), $SiH_2O$. The authors have not been able to isolate this, as it is about as volatile as the hydrogen bromide solution, and, furthermore, polymerises most readily, so that after a few distillations the whole of the original silicon is found in the insoluble residues. The *polymeride* is an amorphous, white solid, which is stable at 300° (vacuum) or in contact with boiling water, but inflames in the air or chlorine, and reacts with sodium hydroxide according to the equation $(SiH_2O)_x + 2NaOH \longrightarrow 2H_2 + Na_2SiO_3$. J. C. W.

**Proof of the Production of Water in the Formation of Salts from Acid and Base.** W. Franck (*Zeitsch. physikal Chem. Unterr.*, **30**, 147; from *Chem. Zentr.*, 1917, ii, 358—359).—In the experiment described by Zeitler (A., 1917, ii, 463), calcium or barium hydroxide should be used, as the alkali hydroxides are never anhydrous. R. V. S.

**The System Lithium Sulphate-Lithium Chloride-Water at 30°.** F. A. H. Schreinemakers and G. M. A. Kayser (*Chem. Weekblad*, 1918, **15**, 120—121).—The solubility of lithium sulphate in water is much diminished by the presence of lithium chloride. A. J. W.

**The Necessity for Applying a New Correction to the Atomic Weight of Silver.** Ph. A. Guye (*J. Chim. phys.*, 1917, **15**, 549—560).—The author discusses the various sources of error, due to the presence of occluded gases and the adherent pellicle of moisture on the metal, in the atomic weight determinations of silver. On the basis of recent work (compare A., 1916, ii, 432), he considers that the atomic weight of silver should be revised to 107·87, and that the correct values for the halogens should be Cl = 35·461, Br = 79·925, I = 126·915. W. G.

**Metallographic Investigation of the System Zinc and Selenium.** Masumi Chikashige and Rokuro Kurosawa (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 245—248).—When zinc and selenium are heated together at a sufficiently high temperature, the compound ZnSe is formed. Zinc selenide has a brilliant yellow colour, $D^{21}$ 5·29, and does not fuse up to 1100°. The fused elements are not appreciably miscible, and the selenide does not dissolve in either. If a fused mixture is allowed to cool, the two free elements and the compound are detectable in the solidified product when examined under the microscope. [See *Ind.*, 153A.] H. M. D.

**Metallographic Investigation of the System Cadmium and Selenium.** Masumi Chikashige and Riichi Hikosaka (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 239—244).—Cadmium and selenium combine to form the compound CdSe, which is infusible up to 1350° and has $D^{16}$ 5·81. The reaction between the elements begins to be appreciable at about 360°, and its velocity increases with rise of temperature. The cadmium selenide does not dissolve in either of the molten elements, which are themselves practically immiscible. When, therefore, a mixture of the two elements is fused and cooled, the product consists of a mixture of cadmium selenide, cadmium, and selenium, which are readily recognised under the microscope. The proportion of the compound in the product depends on the temperature to which the mixture has been heated and on the length of the period of heating. [See *Ind.*, 153A.]

H. M. D.

**The System, Copper Chloride-Lithium Chloride-Water at 30°.** F. A. H. SCHREINEMAKERS and (MISS) A. C. NOORDUYN (*Chem. Weekblad*, 1918, **15**, 118—120).—An application of Schreinemakers's graphic method to solutions containing cupric and lithium chlorides.

A. J. W.

**The Critical Constants of Mercury.** E. ARIÈS (*Compt. rend.*, 1918, **166**, 334—337).—Using the formula previously given (compare this vol., ii, 61) for monatomic vapours, and taking the known vapour pressures of mercury at different temperatures, the author calculates the critical temperature of mercury as 1077° and the critical pressure as 420 atmos., these values being a close approximation to the correct figures.

W. G.

**Preparation, Properties, and Analysis of "White Precipitate."** I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 208—218).—A comparison of the methods for preparing "white precipitate" given in the Dutch, German, English, Belgian, Swiss, and U.S.A. pharmacopœias. The author is of opinion that the Dutch method is the most satisfactory. [See, further, *Ind.*, April.]

A. J. W.

**The Space Lattice of Aluminium.** P. SCHERRER (*Physikal. Zeitsch.*, 1918, **19**, 23—27).—The method described by Debye and Scherrer (A., 1917, ii, 437) for the *X*-ray examination of crystal structure has been applied to finely powdered aluminium. The interference photographs afford evidence that aluminium forms cubic crystals, and that the atoms are arranged according to a simple face-centred lattice. Measurements of the interference patterns give $4{\cdot}07 \times 10^{-8}$ cm. for the length of the edge of the elementary cube. The corresponding values obtained from previous investigations are: copper 3·61, silver 4·06, gold 4·07, and lead $4{\cdot}91 \times 10^{-8}$ cm.

In spite of the close agreement between the values of the lattice constants and of the atomic volumes for aluminium and gold, the two metals do not form a complete series of mixed crystals. This is attributed to the preponderating influence of chemical affinity.

H. M. D.

**The Effect of Great Hydrostatic Pressure on the Physical Properties of Metals.** ZAY JEFFRIES (*J. Inst. Metals*, 1917, **18**, 243—252).—The statement of Hanriot (A., 1913, ii, 112) that metals subjected to hydrostatic pressures of the order of 10,000 kilos. per sq. cm. are permanently hardened without deformation, is contrary to modern views on hardness. A repetition of the experiments, using aluminium and an alloy of aluminium and copper, immersed in light petroleum under pressures up to 12,400 kilo. per sq. cm., shows that no increase in hardness is produced. Hanriot used vaselin, which becomes solid under very high pressures, so that the pressure applied is not hydrostatic. Experiments with the same metals show that a degree of cold deformation, insufficient to cause a noticeable change in the dimensions, produces a marked increase in the hardness as determined by the scleroscope. This explanation is more probable than that of the occurrence of allotropic change in the metal. [See *Ind.*, April.]

C. H. D.

**Metallographic Investigation of the System, Aluminium and Selenium.** MASUMI CHIKASHIGE and TSUGIJI AOKI (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 249—254).—Cooling curve observations show the formation of a compound, $Al_3Se_4$, which melts at about 950°. The formation of this compound by heating the two elements together is frequently accompanied by an explosion unless the mixture contains more than 90% of selenium. The compound crystallises out from all fused mixtures of the two elements, and in accordance with this, the two branches of the compound curve on the freezing-point diagram cover the whole of the region from pure aluminium to pure selenium. The eutectics are therefore very nearly coincident with the freezing points of the two elements. The microcrystalline structure of solidified mixtures is in agreement with the thermal data.

Aluminium selenide decomposes in contact with moist air with the formation of hydrogen selenide and aluminium hydroxide. [See *Ind.*, 153A.]

H. M. D.

**Metallographic Investigation of the System, Tellurium and Aluminium.** MASUMI CHIKASHIGE and JITSUZO NOSÉ (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 227—232).—When aluminium and tellurium are heated together, combination takes place with explosive violence, and the compound $Al_2Te_3$, m. p. 895°, is formed. This telluride forms mixed crystals with tellurium, the series extending from the pure compound (12·4% by weight of aluminium) to a mixture which contains 4·4% of aluminium. On cooling, the $\alpha$-mixed crystals undergo transformation into $\beta$-mixed crystals. The temperature at which this conversion takes place diminishes with increase in the tellurium content, and for the saturated $\alpha$-mixed crystals falls to 541°. The $\beta$-mixed crystals and tellurium co-exist at the eutectic temperature 414°, the eutectic mixture containing 2·8% of aluminium.

The freezing-point curve of the compound $Al_2Te_3$ on the aluminium side is terminated by a eutectic point, in which the telluride and aluminium co-exist in equilibrium. The eutectic mixture contains 97% of aluminium and the eutectic temperature is 621°.

The conglomerates, consisting of the telluride or aluminium and the eutectic, undergo transformation when the temperature has fallen to 551°, with the formation of $Al_5Te$, according to the equation $Al_2Te_3+13Al=3Al_5Te$.

The telluride, $Al_2Te_3$, is energetically decomposed by water or by contact with moist air, with the formation of hydrogen telluride and aluminium hydroxide, according to the equation $Al_2Te_3+3H_2O=3TeH_2+Al_2O_3$. The compound $Al_5Te$ is less readily decomposed, but hydrogen telluride is liberated in contact with water, the reaction being possibly represented by $Al_5Te+H_2O+O_2=TeH_2+Al_2O_3+3Al$.

Microphotographs are given which afford evidence in support of the results obtained by the thermal analysis of the system. [See *Ind.*, 153A.] H. M. D.

**A Criterion for Allotropic Transformations of Iron at High Temperatures.** Kôtarô Honda (*Sci. Rep. Tohoku Imp. Univ.*, 1917, **6**, 213—217).—The transformations of iron consist in part of allotropic changes which take place at a definite temperature and of gradual changes in which the equilibrium condition is a continuous function of the temperature. The available data relating to these transformations show that $A_2$ is of the second type, whilst $A_3$ and $A_4$ are allotropic changes.

In the case of carbon steels, there are in addition the changes designated by $A_0$ and $A_1$, the former representing a gradual change in cementite, and the latter a eutectic transformation of cementite and ferrite which occurs at a definite temperature. H. M. D.

**The Micro-structure of Commercially Pure Iron between $Ar_3$ and $Ar_2$.** W. J. Brooke and F. F. Hunting (*J. Iron Steel Inst.*, 1917, **96**, 233—250).—Armco iron, a basic open-hearth product containing as much as 99·84% Fe, passes through a characteristic brittle range between 900° and 800°, but only during cooling, no change being observed within this range during heating. Quenching experiments show that a eutectic or eutectoid structure appears between these temperatures, but is absent either above or below the brittle range. This constituent resembles pearlite in structure, but is not related to the carbon content, and is also independent of the quantity of oxide in the iron. Heating in hydrogen is without influence on the structure. Similar results are obtained with Swedish iron containing about 0·04% of carbon. [See, further, *Ind.*, 1917, 1096.] C. H. D.

**The Nature of Subsidiary Valencies. XVII. Prediction of the Decomposition Temperatures of Ammines.** Fritz Ephraim and Elias Rosenberg (*Ber.*, 1918, **51**, 130—136).—It was recently shown that the ratio of the temperatures of dissociation for certain pairs of compounds of two elements is roughly constant (A., 1917, ii, 531). If the dissociation points of a number of compounds of one element are known, and the ratio has been determined in the case of one pair of corresponding compounds for another element, then the dissociation temperatures of all the other compounds of the second element can be predicted. This is illustrated further in the case of the hexammines of nickel and cobalt salts. The ratio, or "temperature-modulus of the tension," calculated from the dissociation temperatures of the iodides, is Ni/Co, 1/1·075 (A., 1912, ii, 546). Dividing the known temperatures for other nickel salts by 1·075, therefore, gives approximately the dissociation points for the corresponding cobalt salts. In the cases of the hexammines of the bromides, nitrates, dithionates, chlorides, sulphates, acetates, and hydrogen carbonates (descending order of stability), the calculated values agree with the observed ones within the limits of the experimental errors.

Most of the hexammines mentioned have been described before (A., 1913, ii, 496, 1061), but the following are new: *cobalthexammine nitrate*, by warming the crystalline nitrate in ammonia gas, *dithionate*, *hypophosphite*, *formate*, and *acetate*; the dissociation temperatures are respectively 160°, 157·5°, 51°, 21·5°, and 55·5°. J. C. W.

**Metallographic Investigation of the System, Selenium and Antimony.** MASUMI CHIKASHIGE and MASASUKE FUJITA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 233—237).—Cooling-curve data show that antimony and selenium form a compound, $Sb_2Se_3$, melting at 572°. With antimony, the compound forms a eutectic mixture containing 46·5% of selenium, the eutectic temperature being 497°. The eutectic on the selenium side of the compound corresponds very nearly with pure selenium melting at 211°.

Microscopic investigation of solidified mixtures of the two elements confirm the results obtained in the thermal analysis. [See *Ind.*, 153A.] H. M. D.

## Mineralogical Chemistry.

**Composition of Seleniferous Sulphur.** GLENN V. BROWN (*Amer. Min.*, 1917, **2**, 116—117. Compare A., 1916, ii, 531).—Examination of further specimens of so-called selen-sulphur from various localities (Sicily, Lipari, and New Zealand) by the method of W. Smith (A., 1915, ii, 839) shows the presence of only small amounts of selenium (trace—0·298%). The depth of colour of the material bears no relation to the amount of selenium present; pale yellow specimens may contain more of this element than deep brown ones. L. J. S.

**Epiboulangerite from Montana.** EARL V. SHANNON (*Amer. Min.*, 1917, **2**, 131—132).—Bunches of steel-grey needles and fibrous masses occur with quartz and granular blende in the Iron Mountain mine, near Superior, Montana. Small grains and needles are also scattered through the blende. Associated minerals in small amounts are chalybite, pyrites, and sericite. The fibres are moderately brittle and break across at right angles; the streak is blackish lead-grey. D 6·303. A partial analysis gave Pb 52·74, Sb 20·85%. From these characters, the mineral is provisionally identified as epiboulangerite. L. J. S.

**Mullanite, a New Member of the Jamesonite Group, from Two Localities.** Earl V. Shannon (*Amer. J. Sci.*, 1918, [iv], **45**, 66—70).—In the Iron Mountain mine near Superior, Montana, the new mineral occurs with epiboulangerite (preceding abstract), from which it is indistinguishable in appearance; but it is readily distinguished by its brownish-black streak, that of the epiboulangerite being greyish-black. It here forms long, parallel, steel-grey fibres around and enclosed in a crystal of quartz. In the Gold Hunter mine, near Mullan, in Idaho, forty miles W.N.W. of the former locality, the mineral occurs with quartz and chalybite as fine, matted, wool-like masses of dark grey fibres, and as a compact, steel-grey, fibrous material. The needles are usually flattened and are deeply striated longitudinally; they are terminated by the basal plane, and are probably orthorhombic ($a:b=1:0·835$) with the three pinacoidal cleavages. The thinner fibres are very flexible, whilst the thicker ones are quite brittle. Analysis I, mean of two of material from the Iron Mountain mine, and II, from the Gold Hunter mine, agree with the formula $5PbS,2Sb_2S_3$, corresponding with the silver-lead diaphorite.

| | Sb. | As. | Pb. | Ag. | Cu. | Fe. | S. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 25·71 | 0·25 | 55·05 | nil | nil | trace | 18·82 | 99·83 | 6·274* |
| II. | 24·67 | 0·64 | 53·33 | nil | nil | 1·47† | 18·11 | 98·22 | 6·407 |

* Probably low. † Representing chalybite 3·4% present as impurity.

L. J. S.

**Occurrence of Chalmersite, $CuFe_2S_3$, in the Ore Deposits of Prince of Wales Sound, Alaska.** Bertrand L. Johnson (*Econ. Geol.*, 1917, **12**, 519—525).—This mineral, previously known only as minute crystals from Brazil (A., 1902, ii, 267; 1906, ii, 553), has been found in considerable quantities at eight different localities in the Ellamar district and on Knight Island, in Prince of Wales Sound, where it has been mined as an ore of copper. It is massive, very pale yellow, and shows a conspicuous cleavage with a satiny sheen. It is strongly magnetic, and this property enables it to be separated from the copper-pyrites with which it is intimately intergrown. Analyses by E. T. Allen agree with the formula $CuFe_2S_3$.

| Cu. | Fe. | S. | Sp. gr. |
|---|---|---|---|
| 22·67—23·83 | 40·70—41·92 | 35·09—35·30 | 4·04 |

L. J. S.

**Chalcedony Mistaken for an Iron Sulphate Mineral.** Edgar T. Wherry and Miltiades L. Glenn (*Amer. Min.*, 1917, **2**, 6—7).—Two specimens of orange-brown botryoidal material had been for many years labelled as glockerite in the U.S. National Museum. I is from Pinos Altos, New Mexico, and II from Black Hawk, Colorado. When examined, they were found to be chalcedony, and this is confirmed by analyses I and II. The ferric sulphate is not present as visible enclosures, nor is it extracted by acids; it must be present as sub-microscopic inclusions.

| | $SiO_2$. | $Fe_2O_3$. | $SO_3$. | $H_2O < 110°$. | $H_2O > 110°$. | Total. | Sp. gr. | *n*. |
|---|---|---|---|---|---|---|---|---|
| I. | 94·37 | 3·10* | 1·47 | trace | 1·86 | 100·80 | 2·57 | 1·530 |
| II. | 93·94 | 1·58 | 1·00 | 0·65 | 2·59 | 99·76 | 2·55 | 1·525 |

* Including a minute amount of pyrites.

For pure chalcedony $D = 2·60$ and $n = 1·537$; as shown above, with increasing water there is a corresponding decrease in the values for the density and refractive index. L. J. S.

**Massicot and Litharge, the Two Modifications of Lead Monoxide.** ESPER S. LARSEN (*Amer. Min.*, 1917, **2**, 18—19).—Natural specimens of 'massicot' from Austria and from Kern Co. and San Bernardino Co., California, consist of minute brownish-red scales built up of two minerals with distinct optical properties. The central portion of the plates consists of the yellow orthorhombic modification (nearly colourless under the microscope, optically biaxial and positive, $\beta = 2·61$, birefringence very strong), and the borders of the red tetragonal modification (yellowish-orange under the microscope, optically uniaxial and negative, $\omega = 2·64$, birefringence very strong). It is proposed to restrict the name litharge to the former and massicot to the latter. The border of massicot is probably an inversion product of the litharge. (Compare A., 1915, ii, 59). L. J. S.

**Nomenclature of the Lead Monoxide Minerals.** E. T. WHERRY (*Amer. Min.*, 1917, **2**, 19).—The mineralogical term massicotite for a mineral corresponding with the artificial product massicot was used by D'Achiardi in 1883. Now that the orthorhombic modification of lead monoxide has been recognised as a mineral (see preceding abstract), the name *lithargite* is suggested for the second species. L. J. S.

**Xanthosiderite from Schendlegg, Lower Austria: Formation of Brown "Glaskopf."** H. LEITMEIER and M. GOLDSCHLAG (*Centr. Min.*, 1917, 473—477).—Near the foot of the Raxalp, in Lower Austria, are deposits of iron ore consisting of chalybite carrying small amounts of copper-pyrites. In the level of the Schendlegg mine, the walls are coated with a reddish-brown, unctuous, colloidal material of recent formation. After drying in the air for a few weeks, this shows a concentric, shelly structure and brown colour; the streak is yellowish-brown. Under the microscope, it showed thin scales of brownish-yellow, amorphous material. It then contained 19·70% $H_2O$, corresponding with $Fe_2O_3,2H_2O$—the formula for xanthosiderite. Of this water, 3·93% is lost over sulphuric acid and 8·16% at 100°. The same material after exposure to the air for two years still contained the same quantity of water ($H_2O$ 19·11, $Fe_2O_3$ 80·02, $SiO_2$ 0·47%), but it had by that time acquired a dark blackish-brown colour with metallic lustre on the surface and a dark brown streak. Under the microscope, the material was now seen to have a distinct granular structure and to be crystalline. The colloidal material has thus become gradually converted to the crystalline, brown "Glaskopf." L. J. S.

**Columnar Manganocalcite from Franklin Furnace, New Jersey.** WALLACE GOOLD LEVISON (*Amer. Min.*, 1916, **1**, 5).—This is pinkish-white with a marked columnar structure. It is tough and less brittle than ordinary calcite, and is soluble in cold acid. Analysis gave:

| CaO. | MnO. | FeO. | ZnO. | MgO. | $CO_2$. | Insol. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|
| 38·58 | 11·94 | 0·22 | 0·29 | 4·33 | 39·70 | 4·60 | 99·66 | 2·81 |

L. J. S.

**Proof that Priceite is a Distinct Mineral Species.** ESPER S. LARSEN (*Amer. Min.*, 1917, **2**, 1—3).—The friable, chalky priceite from Curry Co., Oregon, and the compact, nodular pandermite from Asia Minor have often been regarded as impure, massive varieties of colemanite. A determination of the optical constants of these minerals proves that pandermite is identical with priceite ($\alpha=1·572$, $\beta=1·592$, $\gamma=1·594$), and that the latter is distinct from colemanite ($\alpha=1·586$, $\beta=1·592$, $\gamma=1·614$). Priceite is triclinic, $5CaO,6B_2O_3,9H_2O$, and colemanite monoclinic, $2CaO,3B_2O_3,5H_2O$. On the other hand, fine-grained specimens (labelled priceite) of hydrous calcium borate from Californian localities were found to be howlite. L. J. S.

**Vivianite from the Land Pebble Phosphate Deposits of Florida.** THOMAS L. WATSON and STAPLETON D. GOOCH (*J. Washington Acad. Sci.*, 1918, **8**, 82—88).—An examination of a sample of vivianite occurring in a ferruginous or dark yellow, ochreous matrix in a deposit of Florida pebble phosphate. The mineral occurred as light to pale green crystals, D 2·693, an optical examination of which gave the following results: optically (+); $2V$ large; dispersion not strong; $X$ is normal to 010; $Z$ makes an angle of $28°30' \pm 1°$ with $c$. The refractive indices are $\alpha=1·580 \pm 0·003$; $\beta=1·598 \pm 0·003$; $\gamma=1·627 \pm 0·003$. Analysis gave:

| FeO. | $Fe_2O_3$. | CaO. | MnO. | $P_2O_5$. | $TiO_2$. | $SiO_2$. | $H_2O$ (<105°). | $H_2O$ (>105°). | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 32·64 | 9·43 | 0·02 | 0·25 | 29·99 | trace | 0·12 | 11·86 | 15·84 | 100·15 |

The presence of ferric oxide in blue vivianite is due to oxidation, and not to inversion. Oxidation takes place rapidly on fine grinding. The matrix in which the vivianite occurs is not a clay, but an earth composed of the hydroxides of iron and aluminium, chiefly the former, phosphates of calcium, iron, and aluminium, and some free quartz. W. G.

**Mirabilite from the Isle Royale Mine, Michigan.** ALBERT B. PECH (*Amer. Min.*, 1917, **2**, 62—63).—The material, from the Isle Royale copper mine at Houghton, consists of a clear, colourless mass of interlocking fibres with a little clayey matter enclosed. On exposure to the air, it soon crumbles to a white powder. All the water is expelled at 130°. Deducting 5·69% insoluble, the following analysis agrees with the usual formula, $Na_2SO_4,10H_2O$. Mean refractive index, 1·437.

| $Na_2O$. | $K_2O$. | CaO. | $SO_3$. | Cl. | $H_2O$. |
|---|---|---|---|---|---|
| 19·02 | 0·77 | trace | 25·37 | trace | 54·84 |

L. J. S.

**Gilpinite, a New Uranium Mineral from Colorado.** ESPER S. LARSEN and GLENN V. BROWN (*Amer. Min.*, 1917, **2**, 75—79).—The mineral occurs as pale greenish-yellow to canary-yellow aggregates of minute, lath-shaped crystals intermixed with gypsum on pitchblende and copper ore from Gilpin Co., Colorado. The crystals are monoclinic, and show two sets of polysynthetic twin-lamellæ. The optical constants are compared with those of zippeite and uranopilite. The mineral is readily soluble in dilute acids; it is difficultly fusible, and becomes black on heating. $D > 3·32$. The following analysis (19·64% gangue, mainly pitchblende, deducted) gives the formula $RO,UO_3,SO_3,4H_2O$, where $R = Cu, Fe, Na_2$.

| $SO_3$. | $UO_3$. | CuO. | FeO. | PbO. | $Na_2O$. | $K_2O$. | $H_2O$ at 105°. | $H_2O$ at 200°. |
|---|---|---|---|---|---|---|---|---|
| 15·45 | 56·72 | 5·80 | 4·77 | 0·82 | 1·93 | 0·70 | 1·66 | 12·15 |

A specimen labelled uranopilite from Cornwall was found to have optical characters identical with those of the Colorado mineral, and it is also regarded as gilpinite. L. J. S.

**The Probable Identity of Uranothallite and Liebigite.** ESPER S. LARSEN (*Amer. Min.*, 1917, **2**, 87).—Optical examination of three specimens labelled liebigite from Schneeberg, Saxony, and Joachimsthal, Bohemia, and of two specimens labelled uranothallite from the latter locality, gave the following results: optically positive, $2E = 65° \pm 3°$, $2V = 42° \pm 2°$, $\rho > v$, $\alpha = 1·500$, $\beta = 1·503$, $\gamma = 1·537 \pm 0·003$, cleavage normal to $\alpha$. The single analysis of liebigite (for which the formula was deduced as

$$CaO,UO_3,2CO_2,20H_2O)$$

was made in duplicate on only 65 and 85 mg. of material, and although this name has priority, it is rejected in favour of the name uranothallite, which was applied to more completely determined material, and analysed by three authors with the result $2CaO,UO_3,3CO_2,10H_2O$. It is, however, remarked that the original material described as liebigite was not available for optical examination, and it is possible that those examined may really have been uranothallite incorrectly labelled liebigite. L. J. S.

**Pectolite Pseudomorphous after Quartz from West Paterson, N.J.** Miltiades L. Glenn (*Amer. Min.*, 1917, **2**, 43—45).—A small group of crystals collected from a basalt quarry at West Paterson, New Jersey, shows the forms of sharply-developed crystals of quartz, each about ⅜ inch in diameter. They, however, consist entirely of a compact, fibrous material with the optical characters of pectolite. Analysis of the material gave:

| $SiO_2$. | $Al_2O_3+Fe_2O_3$. | CaO. | MgO. | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|
| 53·42 | 0·52 | 32·63 | 2·35 | 7·45 | 3·77 | 100·14 |

L. J. S.

**A New Occurrence of Stevensite, a Magnesium-bearing Alteration-product of Pectolite.** Miltiades L. Glenn (*Amer. Min.*, 1916, **1**, 44—46).—The Hartshorn quarry at Springfield, Essex Co., New Jersey, is in a somewhat altered basalt containing in cavities secondary anorthoclase, quartz, calcite, zeolites, datolite, and pectolite. Some of the pectolite is of the usual type as silky radiations of fine needles, but much of it is altered, the colour becoming pinker and the lustre more waxy towards the ends of the fibres. In the most altered material the colour is white to pink, lustre waxy, translucent; the structure is compact, and the material optically isotropic and amorphous, *n* about 1·50; D 2·15—2·20, H 2½. It is easily fusible to a white enamel, and is decomposed by hydrochloric acid with separation of granular silica. Analysis I is of partly altered material still retaining the pectolite structure, but impregnated by waxy material; and II of the most altered waxy material, apparently homogeneous, although still perhaps containing a few fibres of unaltered pectolite:

| | $SiO_2$. | $Al_2O_3+Fe_2O_3$. | MnO. | CaO. | MgO. | $Na_2O$. | $H_2O(>110°)$. | Total. |
|---|---|---|---|---|---|---|---|---|
| I. | 53·84 | 1·18 | 0·13 | 22·59 | 9·81 | 5·59 | 6·76 | 99·90 |
| II. | 58·03 | 0·37 | 0·03 | 1·61 | 27·66 | 3·73 | 8·45 | 99·88 |

These analyses, when arranged in a series with other analyses of altered pectolites ('walkerite' from Corstorphine Hill, Edinburgh, and 'magnesium pektolith' from Burg, Herborn, Germany), show a gradual passage from the monohydrate of pectolite,

$$HNaCa_2(SiO_3)_3+H_2O,$$

to the monohydrate of talc, $H_2Mg_3(SiO_3)_4+H_2O$. They show a progressive increase in magnesium and water and a decrease in calcium and sodium. The latter formula, to which anal. II approximates, is given as the composition of stevensite. The alteration has no doubt been brought about by the action of magnesium-bearing solutions derived from the weathering of the basalt. L. J. S.

**A Review of Amorphous Minerals.** Austin F. Rogers (*J. Geol. Chicago*, 1917, **25**, 515—541).—The amorphous equivalents of crystalline minerals should be recognised as separate mineral species and given distinctive names. About twenty of the more prominent and well-defined, amorphous minerals (for example, opal, psilomelane, collophane, halloysite, etc.) are discussed. The amorphous cadmium sulphide, probably with adsorbed water, $CdS,xH_2O$, which occurs as a thin, powdery, yellow coating on zinc-blende, is separated from the hexagonal greenockite and named *xanthochroite.*

Intimately associated with the chrysocolla (a microcrystalline or crystallised mineral) of several localties is the amorphous equivalent, to which the name *cornuite* is applied. Cornuite from Copper Mountain, Prince of Wales Island, Alaska, occurs as a banded crust of bluish-green, transparent, glassy material with refractive index 1·549. It is more readily soluble in hydrochloric acid than chrysocolla, and is also somewhat softer. Analysis by G. S. BOHART gave:

| CuO. | $Al_2O_3$. | $SiO_2$. | $H_2O$. |
|---|---|---|---|
| 42·61 | 0·31 | 34·13 | 23·11 |

Here the ratios of both silica and water are somewhat in excess over those required by the chrysocolla formula, $H_4CuSiO_5$, and cornuite is probably a solid solution of cupric oxide, silica, and water, $mCuO,nSiO_2,xH_2O$.

The natural hydrocarbons and glasses are discussed under the term mineraloids. L. J. S.

**Nature of the Water in Zeolites.** GEORG STOKLOSSA (*Diss. Breslau,* 1917, 64 pp.; from *Chem. Zentr.*, 1917, ii, 420—421).—The author has investigated the following seven minerals, and has found in all cases that the water contained in them is in chemical combination: (1) heulandite from Teigarhorn, in Iceland; (2) skolezite from Iceland; (3) natrolite from Bohemia; (4) harmotome from Strontian; (5) chabasite from Nova Scotia; (6) analcime from the Seiseralp; (7) apophyllite from the Seiseralp. Analyses gave:

| | $SiO_2$. | $Al_2O_3$. | BaO | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 1. | 59·66 | 16·37 | — | 6·33 | — | 2·35 | 0·42 | 14·90 | 100·03 |
| 2. | 46·71 | 25·90 | — | 13·70 | — | — | — | 13·64 | 99·95 |
| 3. | 46·95 | 27·06 | — | 0·27 | — | — | 15·97 | 9·58 | 99·73 |
| 4. | 48·51 | 16·44 | 20·19 | — | — | 1·59 | — | 13·79 | 100·52 |
| 5. | 48·12 | 19·27 | — | 9·63 | 2·45 | 3·02 | — | 16·11 | 98·59 |
| 6. | 54·74 | 23·64 | — | 0·32 | — | — | 13·71 | 8·55 | 100·96 |
| 7. | 53·87 | — | — | 23·85 | — | 4·81 | — | 16·24 | 99·47 |

R. V. S.

**A New Occurrence of Ptilolite.** LOUIS H. KOCH (*Amer. Min.*, 1917, **2**, 143—144).—This species, previously known only from Colorado, is described from Challis, Idaho. The material consists of a soft, fluffy mass of minute fibres coating a layer of chalcedonic silica on a weathered basic igneous rock. Analysis gave:

| | $SiO_2$. | $Al_2O_3$. | CaO. | MgO. | $K_2O,Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|
| I. | 81·5 | 8·2 | 1·7 | 0·3 | 1·0 | 7·3 | 100·0 |
| II. | 72·3 | 12·3 | 2·6 | 0·4 | 1·5 | 10·9 | — |

The high value for silica is due to the presence of microscopic, spindle-shaped crystals of quartz to the extent of 31⅓%; deducting this, the results are as under II. Under the microscope the material is seen to consist of well-defined, transparent needles with straight optical extinction; biaxial with large angle and optically negative; refractive indices $\alpha=1{\cdot}475$, $\beta=1{\cdot}477$, $\gamma=1{\cdot}478$. D 2·30. L. J. S.

**A Peculiar Clay from near the City of Mexico.** E. W. Hilgard (*Proc. National Acad. Sci., U.S.A.*, 1916, **2**, 8—12).—The material examined consisted of soil samples from certain unproductive tracts of land on the hacienda Santa Lucia. It has the appearance of a dark grey clay, adheres strongly to the tongue, and becomes very plastic with a little water. D 2·25. When immersed in water it swells up to many times (for one sample as much as thirty-two times) its original volume, forming a coherent, gelatinous mass. The larger part of the material is colloidal, but there are also minute, inseparable grains of calcium and magnesium carbonates. A partial analysis gave:

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | CaO. | MgO. | Ign. | Insol. | $Na_2SO_4$. | $Na_2CO_3$. | NaCl. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| 43·00 | 3·48 | 1·76 | 9·06 | 17·11 | 19·60 | 1·83 | 1·74 | 0·74 | 0·12 | 98·44 |

The material is thus mainly a hydrated magnesium silicate allied to saponite or sepiolite, but it differs from these in being very readily decomposed by acids, even by dilute acetic acid, and in its exceptionally high absorptive power for water. The name *lucianite* is suggested for this new type of magnesian clay. L. J. S.

## Analytical Chemistry.

**Filtering Tube.** William M. Thornton, Jun. (*J. Ind. Eng. Chem.*, 1918, **10**, 132).—The stem of a carbon filter tube is provided with a glass tap, and the top of the tube is closed by a rubber stopper, through which pass the stem of a holder for a filter crucible and an exit tube connected with a pump. The carbon tube serves as a small filter flask; the filtrate collected in this tube is discharged by opening the tap and admitting air through a side-tube on the exit tube. The apparatus is convenient for use in dealing with small quantities of liquid. W. P. S.

**Preparation of N/100 Permanganate Solutions.** J. O. Halverson and Olaf Bergeim (*J. Ind. Eng. Chem.*, 1918, **10**, 119—120).—To prepared permanent $N/100$-permanganate solution 0·40 gram of potassium permanganate is dissolved in 1 litre of re-distilled water, and the solution is heated nearly at boiling point for thirty-six hours under a reflux apparatus. The solution is then cooled, kept overnight, filtered through asbestos, and after three days standardised against $N/50$-oxalic acid solution (0·1261 gram of crystallised oxalic acid per 100 c.c.). The strength of the solution does not vary more than 0·1% per week. [See, further, *Ind.*, 193a.]

W. P. S.

**Suggestions on some Common Precipitations.** GEORGE H. BROTHER (*J. Ind. Eng. Chem.*, 1918, **10**, 129—130).—The following directions are given for obtaining precipitates which are retained by filter paper of moderately close texture. In the case of barium sulphate, the sulphate solution should contain about 1 c.c. of hydrochloric acid (D 1·2) per 200 c.c.; it should be heated to boiling, treated with about one-half the required quantity of barium chloride solution, added drop by drop, and the remainder of the barium chloride is added after the lapse of five minutes. The mixture is ready for filtration after a further fifteen minutes' digestion.

Calcium oxalate is readily obtained in a crystalline state by treating the boiling solution of the calcium salt with an excess of ammonium oxalate, dissolving the precipitate by adding a very slight excess of hydrochloric acid, then adding ammonia drop by drop until the precipitate has formed again, and keeping the mixture hot for thirty minutes.

For the precipitation of ammonium phosphomolybdate, the phosphate solution is rendered ammoniacal, then acidified with nitric acid, heated to boiling, and treated at this temperature with ammonium molybdate solution. When a phosphate is precipitated with magnesia mixture, the precipitate should be dissolved by the addition of hydrochloric acid, the solution heated to boiling, and ammonia then added slowly until a distinctly crystalline precipitate has formed; the mixture is now cooled, one-fifth of its volume of ammonia (D 0·9) is added, and, after fifteen minutes, the precipitate is collected on a filter. W. P. S.

**Reagents for Use in Gas Analysis. VI. The Absorption of Hydrogen by Sodium Oleate.** R. P. ANDERSON and M. H. KATZ (*J. Ind. Eng. Chem.*, 1918, **10**, 23—24. Compare A., 1917, ii, 39).—The sodium oleate reagent containing nickel in suspension, recommended by Bosshard and Fischli for the absorption of hydrogen (A., 1915, ii, 788), is of little use. Amongst the objections to the reagent may be mentioned the time and trouble required for the preparation of the catalyst and the readiness with which it oxidises, the bad keeping properties of the reagent itself, and the slowness of the absorption of the hydrogen. [See further, *Ind.*, 82A.] W. P. S.

**Detection and Estimation of Small Quantities of Free Hydrochloric Acid in the Presence of Chlorides and other Mineral or Organic Acids.** M. ENTAT (*Ann. Chim. anal.*, 1918, **23**, 5—7).—Hydrochloric acid may be determined by the electrometric titration method previously described (A., 1917, ii, 268). *N*-Silver nitrate solution is used for titration, and the hydrochloric acid solution should contain 2% of nitric acid. T. F. B.

**Titration of Chlorides by Volhard's Method.** J. M. KOLTHOFF (*Zeitsch. anal. Chem.*, 1917, **56**, 568—576).—Trustworthy results may be obtained in this method if, as recommended by Schoorl, the titration is interrupted at the first change in colour of the indicator, the mixture then stirred thoroughly, and the titration completed. Rothmund's modification (A., 1909, ii, 932) is less trustworthy. The author finds that it is best to dilute the solution containing the chloride and an excess of silver nitrate to a definite volume, shake the mixture thoroughly, allow the precipitate to settle, and titrate an aliquot portion of the clear solution with thiocyanate. As the silver chloride absorbs about 0·7% equivalent of silver, a corresponding correction of 0·7% must be made on the quantity of chloride found. Chlorides may be detected and estimated in the presence of thiocyanates if the latter be oxidised by treatment with sodium peroxide in sulphuric acid solution (if hydrogen peroxide is used it should be tested previously for the presence of chlorides). W. P. S.

**Estimation of Chlorates and Hypochlorites.** E. Rupp (*Zeitsch. anal. Chem.*, 1917, **56**, 580—586).—Ten c.c. of a solution containing about 0·5% of potassium chlorate and calcium hypochlorite are placed in a stoppered litre flask, diluted to 100 c.c., 2 grams of potassium iodide are added, the mixture is acidified with dilute acetic acid, and, after five minutes, it is titrated with *N*/10-thiosulphate solution; this titration gives the quantity of hypochlorite present. Another portion of 10 c.c. of the solution is also placed in a large stoppered flask, and 1 gram of potassium bromide and 30 c.c. of concentrated hydrochloric acid are added. After fifteen minutes, the mixture is treated with 150 c.c. of 1% potassium iodide solution, shaken, and titrated with *N*/10-thiosulphate solution. The difference between the two titrations corresponds with the amount of chlorate in the solution. W. P. S.

**Action of Sodium Sulphide on Iodine and the Use of the Reaction in Analysis.** Josef Ehrlich (*Zeitsch. anal. Chem.*, 1918, **57**, 21—22).—Pure sodium sulphide solution reacts with free iodine to form sodium iodide; sulphur is liberated at the same time, but re-dissolves in the excess of sodium sulphide added. The iodine in an iodide solution also containing other substances may be estimated by liberating the iodine with potassium permanganate, adding an excess of sodium sulphide, separating the manganese sulphide, etc., by filtration, removing the excess of sulphide in the filtrate by treatment with zinc sulphate, and then precipitating the iodine as silver iodide. W. P. S.

**Estimation of Hypobromite and Bromate, or Hypoiodite and Iodate, in Mixtures of the Same.** E. Rupp (*Zeitsch. anal. Chem.*, 1918, **57**, 16—19).—The method is based on the reaction between hypobromites or hypoiodites and hydrogen peroxide, according to the equation $NaBrO + H_2O_2 = NaBr + H_2O + O_2$. The solution containing hypobromite and bromate is treated with a mixture of hydrogen peroxide and sodium hydroxide solution, the excess of the hydrogen peroxide is then removed by boiling, potassium iodide and sulphuric acid are added, and the iodine liberated by the bromate is titrated with thiosulphate solution. Another portion of the solution is treated directly with potassium iodide and sulphuric acid and titrated with thiosulphate solution. This titration is a measure of the hypobromite and bromate together, and the quantity of hypobromite present is obtained from the difference in the two titrations. A mixture of hypoiodite and iodate is analysed in the same way. W. P. S.

**Estimation of Iodates in the Presence of Bromates.** E. Rupp (*Zeitsch. anal. Chem.*, 1918, **57**, 19—21).—Bromates, when treated with dilute hydrochloric acid, are decomposed gradually with the formation of hydrobromic and hypochlorous acids, whilst iodates are not affected by this treatment. To estimate the two salts when contained in the same solution, a portion of the latter is treated with potassium iodide and sulphuric acid and titrated, after a few minutes, with thiosulphate solution. Another portion of the solution is diluted with water to 50 c.c., 20 c.c. of 12·5% hydrochloric acid are added, and, after one hour, the mixture is treated with 25 c.c. of 3% hydrogen peroxide solution and 15 c.c. of 15% sodium hydroxide solution, boiled for ten minutes, cooled, and titrated with thiosulphate solution after the addition of potassium iodide and sulphuric acid. The first titration gives the quantities of bromate and iodate together, and the difference between the two titrations corresponds with the quantity of bromate present. W. P. S.

**Estimation of Sulphur in Pyrites.** Z. Karaoglanow [with P. and M. Dimitrow] (*Zeitsch. anal. Chem.*, 1917, **56**, 561—568). —After the sulphur has been oxidised to sulphuric acid by heating with a mixture of nitric and hydrochloric acids, or by fusion with sodium carbonate and potassium nitrate, the sulphuric acid may be precipitated directly from the hydrochloric acid solution obtained after separating the silica, previous removal of the iron being unnecessary if the precipitation is carried out under the following conditions. The solution (from 0·5 gram of pyrites), which should contain from 30 to 50 c.c. of 6*N*-hydrochloric acid (free), is diluted to 700 c.c., heated to boiling, and 40 c.c. of hot 10% barium chloride solution diluted previously with 100 c.c. of hot water are added gradually while the mixture is stirred. The precipitated barium sulphate is collected after fifteen hours, washed first with water containing hydrochloric acid and barium chloride, then with hot water, dried, ignited, and weighed. W. P. S.

**Gravimetric Estimation of Sulphuric Acid and Barium as Barium Sulphate. II.** Z. Karaoglanow (*Zeitsch. anal. Chem.*, 1917, **56**, 487—498. Compare this vol., ii, 47).—In the estimation of barium, the presence of nitric acid or a large quantity of hydrochloric acid causes the results obtained to be too low; potassium salts and ferric chloride have the opposite effect. Under equal conditions, the errors in the gravimetric estimation of barium are less than in the estimation of sulphuric acid W. P. S.

**Detection of Selenium in Sulphuric Acid.** Luciano P. J. Palet (*Anal. Soc. Quim. Argentina*, 1917, **5**, 121—123).—Sulphuric acid containing selenium gives an intense violet coloration with aspidospermine. The pure acid does not give this reaction, but in presence of an oxidiser, such as potassium chlorate or lead peroxide, it develops a rose-red coloration. [Compare *Ind.*, 147A.] A. J. W.

**Estimation of Nitrogen in Calcium Cyanamide.** (Mlle.) Bronislava Turkus (*Ann. Chim. anal.*, 1918, **23**, 3—5).—In the estimation of nitrogen in cyanamide by Kjeldahl's method, only thirty minutes' digestion with sulphuric acid is required for the complete decomposition of the cyanamide if the sulphuric acid used is diluted previously with one-fourth of its volume of water; for 1 gram of the sample, 40 c.c. of concentrated sulphuric acid mixed with 10 c.c. of water are required. The digestion must be prolonged for more than thirty minutes if the acid used is weaker or stronger than the concentration given. W. P. S.

**The Microchemical Estimation of Nitrogen.** B. Sjollema and C. W. G. Hesserschy (*Biochem. Zeitsch.*, 1917, **84**, 359—370).—A critical examination of the methods of Bang and of Folin and Denis, with some suggested minor alterations of the details. S. B. S.

**Simple Rapid Method of Estimating the Filtrate Nitrogen in Small Quantities of Blood and of other Body Fluids.** R. Donald (*Quart. J. Med.*, 1917, **11**, 19—29).—One c.c. of blood is mixed with 1 c.c. of a saturated solution of sodium chloride in a mixture of nine parts of 6% sulphuric acid and one part of 6% phosphoric acid. It is centrifugalised, and 1 c.c. of the clear liquid is then transferred to a second centrifugal tube, mixed with 0·1 c.c. of 10% phosphomolybdic acid, and again centrifugalised. Of the final clear, protein-free liquid, 1 c.c. is injected into a solution of sodium hypobromite contained in a Doremus ureometer, and the nitrogen evolved is transferred to a calibrated narrow measuring tube and its volume measured. Attention is directed to the necessity of rapping the ureometer prior to the removal of the nitrogen to the measuring tube in order to liberate a considerable proportion of the gas, which otherwise remains in the gas-supersaturated hypobromite solution. The result is obtained in about forty-five minutes from the commencement of the operations, and is stated to be sufficiently accurate for clinical purposes. H. W. B.

**Estimation of Amino-acid Nitrogen in the Blood.** Seizaburo Okada (*J. Biol. Chem.*, 1918, **33**, 325—331).—The chief point in the new method is the removal of the proteins of the blood by heating with dilute acetic acid, the last traces of protein being removed by shaking with kaolin. The use of alcohol as a precipitant is shown to be undesirable (compare Bock, A., 1917, ii, 159). H. W. B.

**The Estimation of Residual Nitrogen of the Blood.** B. SJOLLEMA and C. W. G. HESSERSCHY (*Biochem. Zeitsch.*, 1917, **84**, 371—377).—Different results are obtained according to whether phosphomolybdic acid, metaphosphoric acid, or trichloroacetic acid is used as precipitant of the proteins. S. B. S.

**Still-head for Use in the Distillation of Ammonia.** A. HUTIN (*Ann. Chim. anal.*, 1917, **22**, 242—244).—The apparatus consists of a bulb with a lower tube which enters the neck of the distillation flask, and an upper tube connected with a receiver; this upper tube extends into the bulb, the portion inside the bulb being constricted and bent upwards. If desired, a wide tube filled with glass beads may be placed between the lower tube of the still-head and the distillation flask. The whole apparatus is made of sheet tin, and its purpose is to prevent any spray from the distillation flask passing over into the receiver. W. P. S.

**Use of Diphenylamine-Sulphuric Acid for Colorimetric Estimations.** J. TILLMANS (*Zeitsch. anal. Chem.*, 1917, **56**, 509—511).—A reply to L. Smith (A., 1917, ii, 217). The use of diphenylamine for the colorimetric estimation of nitric acid is trustworthy if the test solution and the standards are treated in exactly the same way, particularly as regards shaking or stirring.
W. P. S.

**Estimation of Phosphorous, Hypophosphoric, and Phosphoric Acids in Mixtures.** R. G. VAN NAME and WILBERT J. HUFF (*Amer. J. Sci.*, 1918, [iv], **45**, 91—102).—The estimation of phosphorous acid in presence of hypophosphoric and phosphoric acids may be effected by the absorption of iodine in presence of disodium hydrogen phosphate.

The same method may be used for the estimation of hypophosphoric acid if this is hydrolysed in presence of hydrochloric acid as catalyst, producing thereby equimolecular quantities of phosphorous and phosphoric acids in accordance with the equation $H_4P_2O_6 + H_2O = H_3PO_3 + H_3PO_4$.

A mixture of phosphorous, hypophosphoric, and phosphoric acids may be analysed by estimating the phosphorous acid before and after hydrolysis by the iodometric method, and also determining the total phosphoric acid in the solution after oxidation. [See, further, *Ind.*, 147A.] H. M. D.

**The Precipitation of Phosphoric Acid in the State of Ammonium Phosphomolybdate. Estimation of Phosphoric Acid by a Simple Azotometric Method.** J. CLARENS (*Compt. rend.*, 1918, **166**, 259—262).—If the phosphate is precipitated by ammonium molybdate in the presence of sufficient ammonium nitrate, the resultant precipitate contains phosphoric acid and ammonia in the proportions requisite to form triammonium phosphate. The proportions to use should be 0·1 gram of phosphoric anhydride and 100 c.c. of ammonium molybdate containing 15—20 grams of ammonium nitrate. The precipitate is washed with distilled water, and the ammonia present estimated by one of the usual methods, such as distillation with potassium hydroxide.

W. G.

**Estimation of Phosphoric Acid. A Modification of the Citrate Method.** J. Grossfeld (*Zeitsch. anal. Chem.*, 1918, **57**, 28—33).—To avoid the intermediate precipitation of phosphoric acid by molybdic acid, the author proposes a method for the analysis of fertilisers, ashes, etc., in which the calcium is precipitated as oxalate from an acetic acid solution, and, after the removal of the calcium oxalate, the phosphoric acid is precipitated in the usual way as ammonium magnesium phosphate, citric acid being added to prevent precipitation of iron and aluminium. The hydrochloric acid solution (or other solution) of the substance under examination is treated with a few drops of methyl-orange solution and an excess of ammonium oxalate solution, and saturated ammonium acetate or sodium acetate solution is added until the colour of the indicator changes from red to yellow; the mixture is then diluted to 100 c.c., mixed, and filtered through a kieselguhr filter. An aliquot portion of the filtrate is mixed with 5 c.c. of 20% citric acid solution and the phosphoric acid precipitated with magnesia mixture. W. P. S.

**Estimation of Phosphoric Acid, particularly in Superphosphate.** G. Vortmann (*Zeitsch. anal. Chem.*, 1917, **56**, 465—487).—For the direct estimation of phosphoric acid in superphosphate, the most trustworthy method consists in precipitation as ammonium magnesium phosphate after the calcium has been removed as oxalate and the iron as sulphide; the presence of ammonium oxalate, ammonium molybdate, and ammonium sulphide does not interfere with the precipitation. If aluminium salts are present, the quantity of magnesia mixture used should be increased. When the phosphoric acid is precipitated with molybdic acid solution before it is converted into ammonium magnesium phosphate, the precipitation may be made equally well from a nitric, hydrochloric, or sulphuric acid solution. Molybdic acid solution containing pyridine is a very sensitive reagent for the detection of traces of phosphoric acid; it will detect 0·01 mg. of $P_2O_5$ in 10 c.c. of solution, whilst the limit for molybdic acid containing nitric acid is about 0·1 mg. of $P_2O_5$ in 10 c.c. The phosphoric acid in superphosphate can also be precipitated as a basic mercury compound by means of yellow mercuric oxide; this compound is then decomposed with sodium sulphide, and the phosphoric acid precipitated as ammonium magnesium phosphate. Precipitation as calcium triphosphate is untrustworthy. [See also *Ind.*, 160A.]

W. P. S.

**Use of Textile Fibres in Microscopic Qualitative Chemical Analysis. II. Detection of Boron by means of Turmeric Viscose Silk Fibres. III. Detection of the Heavy Metals by means of Zinc Sulphide Wool Fibres.** E. M. Chamot and H. I. Cole (*J. Ind. Eng. Chem.*, 1918, **10**, 48—50. Compare A., 1917, ii, 576).—Viscose silk fibres dyed with turmeric are useful for the detection of very small quantities of boric acid; a reaction may be obtained with one drop of solution containing 0·000025 mg. of boron. Wool fibres, free from fat and treated with sodium sulphide and zinc acetate, are suitable for the detection of heavy metals, the coloration obtained indicating the metal present. [See, further, *Ind.*, 75A.] W. P. S.

**Rapid Organic Combustion.** P. A. Levene and F. W. Bieber (*J. Amer. Chem. Soc.*, 1918, **40**, 460—462).—The procedure adopted in the authors' laboratory is fully described, with diagrams. Cerium dioxide is used as a catalyst, and from the first weighings to the final ones, the combustion requires only about forty-five minutes. J. C. W.

**Micro-analysis of Organic Substances.** J. V. Dubsky (*Ber.*, 1917, **50**, 1709—1713).—An account of recent experiences and improvements of micro-methods of combustion, made in the university laboratory at Zurich, where all analyses are now performed with small quantities of material. For the combustion of halogeno-nitro-compounds, the tube contains a 5 cm. layer of pieces of fine silver wire, then a 16 cm. layer of a mixture of copper oxide and lead chromate, then another short layer of silver, and finally the boat. The preliminary decomposition is carried out with the oxygen supply cut off, and if the compound is very poor in hydrogen (for example, trichlorodinitrobenzene) it is found best to adopt Benedict's method (A., 1900, ii, 439) and place before the boat another boat containing a weighed amount of pure benzoic acid, naphthalene, or sugar, in order to reduce some of the copper oxide. [See also *Ind.*, April.] J. C. W.

**Electrical Combustion Furnaces for Micro-analyses.** J. V. Dubsky (*Ber.*, 1917, **50**, 1713—1717).—A description of a platinum resistance and a chromium–nickel resistance furnace designed at the author's instigation for use with silica combustion tubes. [See *Ind.*, April.] J. C. W.

**The Eggertz Test for Combined Carbon in Steel.** J. H. Whiteley (*Iron Steel Inst. Carnegie Schol. Mem.*, 1917, **8**, 1—101).—Small quantities of carbon dioxide may be accurately estimated by absorbing in an ammoniacal solution of barium chloride (McFarlane and Gregory, A., 1906, ii, 802), and an apparatus is described by the use of which the carbon in steel may be estimated by wet combustion or the weight of carbon dioxide evolved during the Eggertz colour test may be determined. This gas is given off, at a decreasing rate, during several hours' heating, and the quantity obtained in a given time is closely proportional to the carbon content of the steel, irrespective of its heat treatment, the only exceptions being austenitic steels. The other volatile products of the reaction include hydrogen cyanide and hydrocarbons, the 'missing' carbon remaining in solution, as shown by oxidation with permanganate. A 1% carbon steel yields, in the first ten minutes' boiling with nitric acid, 22% of its carbon as carbon dioxide, 5—10% as hydrogen cyanide, and 2—3% as hydrocarbons.

The colouring matter of the brown solution is colloidal. When steel is dissolved in nitric acid kept cool by water, a black precipitate forms in all cases in which carbide particles are visible in the section etched with sodium picrate. This precipitate becomes brown later, especially on warming, and later this changes to a brown solution. The particles first formed have the form of the carbide. Quenched steels yield the solution directly. On dialysis, a substance passes through the membrane, which has an orange colour in concentrated solution, but becomes green on dilution. The colour is not merely that of the organic substances present, but depends on the reaction of these with iron. With further heating, the green substance changes to a colourless or only slightly coloured substance. The proportions of the coloured products depend on the electro-chemical conditions of solution, and cold-worked steels give a deeper colour. The tints given by different steels are more easily matched if sulphuric acid be added. For 0·5 gram of steel, 10 c.c. of nitric acid (1·2) are used, and, after boiling for fifteen minutes, 15 c.c. of sulphuric acid (1 : 3 by volume) are added. [See, further, *Ind.*, 1917, 1097.] C. H. D.

**Gravimetric Estimation of Potassium by Sodium Cobaltinitrite.** C. V. Garola and V. Braun (*Ann. Falsif.*, 1917, **10**, 572—575).—The reagent used consists of 28·6 grams of cobalt nitrate and 50 c.c. of glacial acetic acid dissolved in 500 c.c. of water, and 180 grams of sodium nitrite also dissolved in 500 c.c. of water; these two solutions are mixed twenty-four hours before use and then filtered. The mixed reagent keeps for a few days only. Twenty-five c.c. of the potassium salt solution (containing about 0·250 gram of potassium chloride and free from other bases except sodium) are treated in a stoppered flask with 25 c.c. of the reagent, and, after about eighteen hours, the precipitate is collected on an asbestos filter, washed with 10% acetic acid, then once with 95% alcohol, dried at 100°, and weighed. The precipitate contains 20·74% of $K_2O$. The method is trustworthy for the estimation of potassium in fertilisers, soils, wines, etc. Ammonium salts should be removed previously by ignition and other bases by treatment with sodium carbonate and filtration. [See also *Ind.*, 168A.]
W. P. S.

**Estimation of Potassium and Sodium as Chlorides through the use of the Refractometer.** B. A. Shippy and G. H. Burrows (*J. Amer. Chem. Soc.*, 1918, **40**, 185—187).—The refractive index at 25° of a 20% sodium chloride solution is 1·36829, whilst that of a 20% potassium chloride solution is 1·35992. If, therefore, the refractive index of a 20% solution of the mixed chlorides be determined, the approximate quantities of the two salts can be found by a simple calculation. [See also *Ind.*, 168A.]
W. P. S.

**A Proximate Method for the Estimation of Rubidium and Cæsium in Plant Ash.** W. O. ROBINSON (*J. Ind. Eng. Chem.*, 1918, **10**, 50—51).—After removal of phosphoric acid, calcium, magnesium, etc., the mixed alkali chlorides are fractionally precipitated with platinum chloride. The potassium, rubidium, and cæsium platinichlorides are collected, reduced in hydrogen and the resulting chlorides treated with concentrated hydrochloric acid. The solution thus obtained, containing all of the rubidium and cæsium chlorides and a large amount of potassium chloride, is then compared spectroscopically with standard solutions containing known amounts of rubidium, cæsium, and potassium chlorides, and prepared under the conditions given. [See, further, *Ind.*, 76A.] W. P. S.

**Colloido-chemical Methods for Estimating the Hardness of Water.** L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 149—155).—The surface tension of soap solutions is diminished considerably by addition of small amounts of alkali hydroxides, but the addition to such alkaline solutions of small amounts of calcium or magnesium salts increases the surface tension. These facts might form a basis for a method for determining the hardness of water.
S. B. S.

**Estimation of Zinc by Schaffner's Method.** V. HASSREIDTER (*Zeitsch. anal. Chem.*, 1917, **56**, 506—509. Compare A., 1917, ii, 509).—In any of the modifications of this method, the precipitation of the iron (whether it be a single, double, or treble precipitation), should be carried out under conditions which will minimise the retention of zinc. It is advisable to make a comparison precipitation at the same time, using a definite quantity of iron and zinc. The iron precipitate should be tested for the presence of zinc. [See also *Ind.*, 168A.] W. P. S.

**Estimation of Zinc on Galvanised Iron.** O. BAUER (*Stahl u. Eisen*, 1915, 734; from *Ann. Chim. anal.*, 1918, **23**, 21).—A measured and weighed piece of the metallic sheet is treated with a solution containing 2 grams of sulphuric acid and 2 grams of arsenic trioxide per litre; this solution dissolves the zinc readily, but does not attack the iron. When evolution of hydrogen ceases, the remaining sheet of iron is removed from the solution, washed, dried, and re-weighed. This method can be used only with galvanised iron prepared electrolytically; when it is made by the hot dipping process, an iron–zinc alloy is formed between the layers of iron and zinc, and this alloy dissolves in the reagent. The presence of iron in the solution indicates that the galvanised iron had been made by the hot process. W. P. S.

**Estimation of Lead as Phosphate and its Separation from Antimony.** G. VORTMANN and A. BADER (*Zeitsch. anal. Chem.*, 1917, **56**, 577—580).—The solution, containing about 0·5 gram of lead nitrate, is treated with 5 grams of tartaric acid, then rendered slightly ammoniacal, heated at 80°, and 100 c.c. of 10% ammonium phosphate solution are added. The mixture is kept at 70—80° for sixteen hours, then cooled, the precipitate collected, washed with dilute ammonium nitrate solution, dried, ignited at a low temperature, and weighed. If antimony is present, the quantity of tartaric acid used is correspondingly increased; antimony is not precipitated under these conditions, and may be estimated as sulphide in the filtrate from the lead phosphate precipitate. The method yields trustworthy results and is useful for the analysis of "hardened" lead. W. P. S.

**Separation of the Copper Group from the Arsenic Group, with Especial Reference to the Identification of Arsenic.** M. CANNON SNEED (*J. Amer. Chem. Soc.*, 1918, **40**, 187—191).—The method depends on the solubility of mercury, arsenic, antimony, and tin sulphides in a solution prepared by saturating a 12% sodium hydroxide solution with hydrogen sulphide and adding to each litre 400 c.c. of 40% sodium hydroxide solution. Lead, bismuth, copper, and cadmium sulphides remain insoluble. The solution containing the soluble sulphides is treated with ammonium carbonate to precipitate the mercury; arsenic, antimony, and tin sulphides are precipitated by hydrochloric acid, and the antimony and tin sulphides are separated by solution in warm concentrated hydrochloric acid. The arsenic sulphide is dissolved in ammonia, oxidised with nitric acid, and the solution at 80° treated with an excess of ammonium molybdate. The latter yields a yellow precipitate with the arsenic, and will detect as little as 1 part of arsenic in 225,000 parts of water. [See, further, *Ind.*, April.] W. P. S.

**New Methods for the Estimation of Copper, Zinc, Cadmium, Nickel, and Cobalt.** ADOLPHE CARNOT (*Compt. rend.*, 1918, **166**, 245—251).—To a solution containing any one of these metals, sodium carbonate in slight excess is added in the cold until it is just alkaline. The precipitate formed is then redissolved by the addition of just sufficient ammonium hydroxide, or, in some cases, ammonium carbonate, and the liquid is boiled, usually for five minutes, until precipitation is complete. The precipitate is washed, dried and ignited, and weighed as the oxide, or reduced and weighed as the metal. If the amount of precipitate obtained is very small, it is dissolved in a little nitric acid, the solution evaporated to dryness with a little sulphuric acid, and the metal weighed in the form of its anhydrous sulphate. In every case, it is essential to ensure the absence of all ammonium salts prior to the precipitation with sodium carbonate. W. G.

**New Separations of the Five Metals of the Group Soluble in Ammonia.** ADOLPHE CARNOT (*Compt. rend.*, 1918, **166**, 329—333. Compare preceding abstract).—If copper and zinc are present together in solution, they are precipitated and weighed as their combined oxides (*loc. cit.*), and these are then heated in a current of hydrogen. The zinc volatilises as formed, and the residual copper is weighed. With a mixture containing copper, nickel, and zinc, the copper is first precipitated from the boiling acid solution by the addition of sodium thiosulphate and weighed as its sulphide. From the filtrate, the nickel and zinc are precipitated and weighed as the mixed oxides, these being then reduced in hydrogen and the nickel weighed. For an alloy of zinc and cadmium, the metal is dissolved in nitric acid and the solution evaporated nearly to dryness, and then diluted to 150—200 c.c. Sodium carbonate is added until the liquid is alkaline, and then ammonium sesquicarbonate and a little ammonia, the liquid being heated to just below 100° until it no longer smells of ammonia. The cadmium carbonate is washed by decantation with ammonium carbonate solution until free from zinc, and then ignited and weighed as cadmium oxide. The zinc is estimated in the filtrate by Meunier's method (compare A., 1897, ii, 464).

Cobalt may be separated from nickel, when in solution with it, by precipitation with ammonium sulphide in the presence of an alkali oxalate. The nickel passes through in solution on filtering, and is precipitated from the filtrate as nickel sulphide by boiling it with acetic acid. This method also applies to the separation of copper and nickel if an alkali sulphide is used in place of ammonium sulphide.

By a combination of these methods, the five metals if present in solution together may be separated and estimated. W. G.

**The Examination of Mercury Fulminate and the Analysis of Mixtures for Percussion Caps.** Paul Nicolardot and Jean Boudet (*Compt. rend.*, 1918, **166**, 258—259).—Free mercury may be detected in the fulminate by shaking 1 gram of the latter with 100 c.c. of a 5% solution of ammonium thiosulphate. All the fulminate dissolves and leaves the mercury as a grey powder or in metallic globules, which can, if necessary, be weighed.

For the examination of detonating mixtures, the percussion caps are treated first in the cold for two hours, and then at 60° for one hour with yellow ammonium sulphide. The mercury fulminate is converted into mercury sulphide, which is filtered off along with any powdered glass present. To the filtrate, ammonium sulphite is added, and the antimony sulphide which separates is collected and weighed. In the filtrate, the alkali metals are estimated in the usual way. Any chlorate or nitrate in the mixture is extracted with cold water and estimated in the usual manner. Any copper present, owing to the attack of the metal of the caps, will come down with the antimony sulphide, and may be estimated electrolytically after calcining the sulphides and extracting them with nitric acid. W. G.

**Estimation of Manganese in Steel in the Presence of Chromium and Vanadium by Electrometric Titration.** G. L. Kelley, M. G. Spencer, C. B. Illingworth, and T. Gray (*J. Ind. Eng. Chem.*, 1918, **10**, 19—23).—The manganese is oxidised to permanganate by sodium bismuthate or ammonium persulphate, and the permanganate then titrated with mercurous nitrate solution. The solution to be titrated should contain about 50 c.c. of sulphuric acid (D 1·58) per 200 c.c. of water, and the temperature should be 20°. The end-point of the titration, as observed on the electrometric apparatus, is sharp and is not affected by the presence of chromates or vanadates. [See, further, *Ind.*, 92A.] W. P. S.

**Analysis of Tin Ores.** T. F. Golick (*Eng. Min. J.*, 1916, 827; from *Ann. Chim. anal.*, 1917, **22**, 248).—The ore is fused with a mixture of potassium carbonate and sulphur, the mass, when cold, is extracted with hot water, and the solution filtered. The filtrate is then evaporated with the addition of sulphuric acid and heated until sulphuric acid fumes are evolved, the residue treated with hydrochloric acid and hydrogen peroxide to insure complete conversion of the tin into stannic chloride, and the tin precipitated as sulphide. After the precipitated sulphide has been collected and washed, it is treated with a known quantity of potassium iodate in the presence of concentrated hydrochloric acid, and the excess is titrated with potassium iodide solution; the reaction proceeds according to the equation: $SnS_2 + KIO_3 + 6HCl = SnCl_4 + S_2 + KCl + ICl + 3H_2O$. W. P. S.

**Detection of Small Quantities of Vanadium in Water.** Victor L. Meaurio (*Anal. Soc. Quim. Argentina*, 1917, **5**, 185—189).—A solution of 0·2 gram of diphenylamine in 100 c.c. of water in presence of hydrochloric acid gives a violet coloration with aqueous solutions of vanadium compounds. The coloration is unaffected by the presence of nitrates, iron, or titanates, and the test will detect the presence of vanadates in solutions of 0·0002% strength. [Compare *Ind.*, April.] A. J. W.

**The Estimation of Vanadium in the Presence of Molybdenum by means of Titanous Chloride.** A. Travers (*Compt. rend.*, 1918, **166**, 289—290. Compare A., 1917, ii, 545).—In using the method previously described (*loc. cit.*), it is now noted that if the indicator, potassium thiocyanate, is added before the titanous chloride, the vanadic acid is reduced first, and when this action is complete, the molybdic acid is reduced. Thus vanadium and molybdenum in steels may be estimated by carrying out the method for the two together, as already described (*loc. cit.*), and then in another portion estimating the vanadium alone by adding the thiocyanate first and running in the titanous chloride from a burette until an end-point is reached. W. G.

**Antimony Dioxide.** Julius von Szilàgyi (*Zeitsch. anal. Chem.*, 1918, **57**, 23—28).—Antimony dioxide may be prepared by heating the pentoxide at bright redness or by oxidising antimony with concentrated nitric acid and heating the resulting oxide at dull redness until constant in weight. When heated with concentrated hydrochloric acid and potassium iodide, antimony dioxide liberates iodine; the reaction proceeds according to the equation: $2SbO_2 + 6HCl + 2HI = 2SbCl_3 + 4H_2O + I_2$. The iodine may be separated by distilling the mixture; if the distillate is collected in a receiver containing potassium iodide solution, titration with thiosulphate solution will give the quantity of antimony dioxide present. Metastannic acid does not liberate iodine from potassium iodide under the above conditions, but the reaction is of little practical use for the estimation of antimony in the presence of tin, since alloys of these two metals usually contain other metals which interfere.

W. P. S.

**Colorimetric Estimation of Bismuth (in Copper).** H. A. B. MOTHERWELL (*Eng. and Min. J.*, 1917, **104**, 1091—1092; from *J. Soc. Chem. Ind.*, 1918, **37**, 92A).—The copper is dissolved in nitric acid, and the cold diluted solution treated with sodium carbonate until a small quantity of the copper is precipitated; this precipitate will also contain all the bismuth. After six hours, the precipitate is collected, dissolved in hydrochloric acid, the copper and bismuth are separated as sulphides, and these are dissolved in nitric acid. To the solution are added 5 c.c. of lead nitrate solution (13·5 grams per litre), the mixture is nearly neutralised with ammonia, treated with an excess of ammonium carbonate, boiled, cooled, the precipitate collected and dissolved in nitric acid, and the precipitation is repeated. If much copper is still present, dilute potassium cyanide solution must be added until the coloration has nearly disappeared, and the precipitate is then washed until free from copper. The precipitate is dissolved in a small quantity of nitric acid, the solution evaporated, the residue dissolved in three drops of nitric acid and 5 c.c. of water, the solution diluted to 25 c.c., and made up to 50 c.c. with 1·7% potassium iodide solution. The coloration obtained is at once compared with that given by a known amount of bismuth under the same conditions and in the presence of 5 c.c. of the lead nitrate solution.

W. P. S.

**The Estimation of Humus by means of a Simplified Procedure of Elementary Analysis.** A. JAKOBSEN (*Zhur. Optyn. Agron.*, 1916, **17**, 93—98; *Expt. Stat. Rec.*, **36**, 614; from *Physiol. Abstr.*, 1918, **2**, 629—630).—The humus in soils is estimated by a combustion method, using platinised asbestos as a catalyst. From 1 to 25 grams of material may be used, and the oxidation is complete in thirty minutes. It is claimed that the method is as satisfactory as the more complex one of Gustavson.

W. G.

**Determination of the Concentration of the Hydrogen Ions in Acid Liquids. Application to Wines.** MARCEL DUBOUX (*J. Chim. Phys.*, 1917, **15**, 473—501).—Two methods are described, namely, a graphic method and a method of calculation, the latter giving the more precise results.

In the first method, a neutralisation curve is drawn, plotting the conductivity of the solution against the volume of standard alkali added, the wine being previously diluted with water in the proportion of 1 : 4 or 3 : 97 by volume, according as the amount of alkali required to neutralise 1 litre of it, as determined volumetrically, is less or greater than 110 c.c. *N*-sodium hydroxide. The tangent to the curve at the neutralisation point is drawn, and the distance $x$ from its point of intersection with the ordinate axis (conductivity) to the curve along the axis is measured. Then $[H^{\cdot}]=x/0{\cdot}291$, or $x/0{\cdot}157$, according to the dilution used.

In the method of calculation, it is necessary to determine (1) the volume of *N*-sodium hydroxide required to neutralise 5—5·2 c.c. of the wine; (2) the percentage of alcohol by volume in a mixture of 1 c.c. of wine to 4 c.c. of water; (3) the specific conductivity of the wine before and after the addition of the volume of alkali as determined in (1). Formulæ are given for the calculation of the hydrogen ion concentration from these data. W. G.

**Volumetric Estimation of Formic Acid in the Presence of Hydroxides, Carbonates, Oxalates, and Acetates.** F. Tsiropinas (*J. Ind. Eng. Chem.*, 1917, **9**, 1110—1111).—The solution, containing from 2·5 to 5 grams of formic acid, together with carbonates, oxalates, and acetates, is boiled for a few minutes, rendered alkaline with sodium hydroxide, and treated with a quantity of calcium chloride sufficient to precipitate the carbonates and oxalates. The mixture is filtered, the filtrate diluted to 250 c.c., and 50 c.c. are acidified with sulphuric acid and boiled in a flask with 400 c.c. of chromic acid solution (50 grams of sodium dichromate, 80 c.c. of concentrated sulphuric acid, and 500 c.c. of water) for fifteen minutes, the flask being connected, through a reflux apparatus, with a gas-measuring tube filled with water. When carbon dioxide ceases to collect in the measuring tube, the volume of the gas is observed, and its weight calculated into formic acid. Acetates, if present, do not interfere, as they are not oxidised by chromic acid. With pure sodium formate, the method yields 99·6% of the formic acid present. W. P. S.

**Estimation of Acetic, Propionic, and Butyric Acids.** R. D. Crowell (*J. Amer. Chem. Soc.*, 1918, **40**, 453—460).—Various principles underlying possible methods for separating the lower aliphatic acids are discussed, and a procedure is described which depends essentially on the fact that most of the butyric acid and some propionic acid can be extracted by means of light petroleum (b. p. 150—300°) after saturating the solution under examination with calcium chloride and a little potassium chloride. The total acidity and weight of sodium salts, dried at 200°, are first determined, and then the acidity and salt weight of the light petroleum extract. The first salt weight minus the sodium acetate equivalent gives the total weight of $-CH_2$ groups, and the second minus the sodium propionate equivalent gives the weight of $-CH_2$ groups present as butyric acid. A correction for the solubility of butyric acid in the calcium chloride solution, etc., also requires to be made. [See, further, *Ind.*, April.] J. C. W.

**Detection and Estimation of Butyric Acid.** G. Denigès (*Ann. Chim. anal.*, 1918, **23**, 27—31).—Five c.c. of a butyric acid solution are mixed with 5 c.c. of hydrogen peroxide solution (0·01 vol. for each 0·01 gram of butyric acid per litre) and 1 c.c. of ammonium ferrous sulphate solution (5 grams of ammonium ferrous sulphate and 10 c.c. of 10% sulphuric acid per 100 c.c.). The mixture is heated at 70° for five minutes, then treated with six drops of sodium hydroxide solution, cooled, filtered, and 5 c.c. of the filtrate are mixed with three drops of sodium hydroxide solution, three drops of 5% sodium nitroprusside solution, and a slight excess (0·5 c.c. or more) of acetic acid. A red coloration develops, its intensity depending on the quantity of butyric acid present. The amount of the acid in the solution may be estimated colorimetrically by comparison with standards under the same conditions. The method may be applied to the estimation of butyric acid in mixtures, organic fluids, etc., after the acid has been separated by distillation or extraction. W. P. S.

**Estimation of Lactic Acid in the Presence of other Organic Acids.** P. Szeberényi (*Zeitsch. anal. Chem.*, 1917, **56**, 505—506).—Lactic acid, when heated with chromium trioxide and sulphuric acid, yields acetic acid, carbon dioxide, and water; if the oxidised mixture is then distilled, the quantity of acetic acid in the distillate is a measure of the lactic acid present. The results obtained are slightly too low, since about 3% of the lactic acid is converted directly into carbon dioxide and water. Under the above conditions, tartaric acid, malic acid, citric acid, and oxalic acid are oxidised directly to carbon dioxide. Volatile acids, alcohol, acetone, and esters must be removed previously by distillation. A small portion of the lactic acid also distils over, and this quantity may be estimated approximately from the acidity and the molecular weights of the acids in the distillate. [See also *Ind.*, 165A.] W. P. S.

**Detection and Estimation of Small Quantities of Hydrocyanic Acid.** J. M. Kolthoff (*Zeitsch. anal. Chem.*, 1918, **57**, 1—15).—Of the various reactions used for the detection of hydrocyanic acid, that depending on the formation of ferrocyanide is the only one which is characteristic and trustworthy. In using this reaction for the colorimetric estimation of small quantities of hydrocyanic acid, it is important to have exactly the same quantities of reagents in both the test and comparison solutions. The thiocyanate reaction (compare A., 1916, ii, 455) may be used for the purpose if it is remembered that certain body fluids (saliva, stomach contents, etc.) may already contain thiocyanate; in such cases, the hydrocyanic acid may be separated by the aeration-distillation method. The picric acid, guaiacum, phenolphthalein, silver, and iodine–starch reactions are untrustworthy, since many substances other than hydrocyanic acid give similar reactions. In dealing with pure hydrocyanic acid, the sensitiveness of the tests (expressed in mg. of CN per litre) is as follows: ferrocyanide, 2; thiocyanate, 0·1; picric acid, 1; guaiacum, 0·004; phenolphthalein, 0·05; silver, 0·03; iodine-starch, 0·1. W. P. S.

**Detection of Picric Acid by Ferrous Tartrate Reagent.** RUPEAU (*Ann. Chim. anal.*, 1918, **23**, 15—16).—The author claims to have been the first to use ferrous sulphate–tartaric acid solution, often called Le Mithouard's reagent, for the detection of picric acid (compare A., 1917, ii, 158). W. P. S.

**Detection of the Poisons which can be Extracted with Ether from the Acid Aqueous Solution in the Stas-Otto Process (Picric Acid, Picrotoxin, Antipyrin).** O. TUNMANN (*Apoth. Zeit.*, 1917, **32**, 441—443, 447—448; from *Chem. Zentr.*, 1917, ii, 499—501. Compare A., 1917, ii, 551).—This is a continuation of the papers referred to. *Picric acid.*—The sublimates are homogeneous, colourless, or even yellow. Typical crystals cannot be reckoned on even after recrystallisation from water or alcohol. Hydriodic acid dissolves the sublimate at once, but no crystals are formed. Zinc chloroiodide dissolves rich sublimates only on warming; on cooling, large, yellow prisms and flat, prismatic crystals are deposited; they show strong pleochroism and extinction parallel to the long axis. Bromine–potassium bromide solution acts similarly, but the prisms are less regular and not pleochroic. On the whole, reactions like the *iso*purpuric acid reaction, the picramic acid reaction, and the dyeing of wool are most satisfactory for these microchemical purposes.

*Picrotoxin.*—The picrotoxin sublimes at 215—225° for the most part. The sublimate exhibits no crystals, but only drops, and crystallisation could not be brought about. Zinc chloroiodide and hydriodic acid yield no reaction products. Nitric acid dissolves the sublimate, but produces no coloration. Rich sublimates yield good crystals of picrotoxin when treated with hydrochloric acid, but it is better to apply 5% ferric chloride solution for this purpose, because this distinguishes picrotoxin sublimates from those of antipyrin. The sublimate and the solution are heated under a cover glass until bubbles appear; on cooling, typical pentagonal tablets can be observed. They are colourless, the large ones polarise in variegated shades and show oblique extinction. If the sublimate under the cover glass is treated with a drop of bromine–potassium bromide solution and heated, colourless prisms of bromopicrotoxinin are formed on cooling. These crystals are monoclinic, and can also be obtained by the action of bromine water.

*Antipyrin.*—The residues from the ethereal extraction of the acid solution yield only traces of antipyrin, because the greater quantity of this substance is extracted only when the solution is alkaline. The sublimates at first consist of drops, which eventually form groups of radially arranged, flat, prismatic crystals, which polarise strongly. These antipyrin deposits yield deep red drops with hydrogen iodide, shining droplets with zinc chloroiodide, and droplets also with bromine–potassium bromide solution. The colour reactions ordinarily used are evident even with the smallest quantities without the aid of a microscope. Two antipyrin reactions which yield decisive crystalline precipitates are to be found in the formation of nitrosoantipyrin and ferripyrin respectively. In the former case, the sublimate is dissolved in a drop of water and treated successively with a drop of 10% sodium nitrite solution and a drop of acetic acid. The green solution deposits doubly refractive, dichroic crystals, or, if it is heated, long, yellow prisms. The ferripyrin reaction is carried out by heating the sublimate with a drop of 5% ferric chloride solution under a cover glass until bubbles are formed; on cooling, orange-yellow crystals are deposited, mostly 30—50 $\mu$ (sometimes 80 $\mu$) long, which show yellow shades in polarised light. The reaction distinguishes antipyrin from salipyrin. In the case of salipyrin, the sublimate consists of groups of bent needles. Addition of ferric chloride produces a violet solution which remains on heating, and no crystals are deposited unless too high a temperature has been used for the sublimation. In this case, a mixture of crystals of ferripyrin and salicylic acid may be observed. R. V. S.

**Microchemistry of some Opium Alkaloids.** L. VAN ITALLIE and J. VAN TOORENBURG (*Pharm. Weekblad*, 1918, **55**, 169—178). —An account of tests applicable to the alkaloids *pseudo*-morphine, protopine, tritopine, cryptopine, laudanine, laudanidine, and laudanosine. [See, further, *Ind.*, April.] A. J. W.

**Modification of the Ehrlich Indole Reaction in Bacterial Cultures.** W. NOWICKI (*Wien. klin. Woch.*, 1917, **30**, 983; from *Chem. Zentr.*, 1917, ii, 498).—The culture, which should contain 8—10 c.c. of peptone water, is treated with 1 c.c. of Ehrlich's reagent and two drops of 40% formaldehyde solution. On shaking, a reddish-violet coloration appears, and by addition of alcohol the solution may be made suitable for colorimetric examination. R. V. S.

**Analysis of Blood and Urine.** O. I. LEE (*St. Luke's Hosp. Med. and Surg. Rep.*, 1917, **4**; from *Physiol. Abstr.*, 1918, **2**, 587). —A mixture, prepared by adding three parts of amyl alcohol to seven parts of phenyl ether, is advocated for the prevention of foaming in analytical work. A colorimetric method for the estimation of iron in urine is described, the iron being precipitated with ammonium persulphate and ammonia, incinerated, and the ash moistened with potassium thiocyanate. The iron content of normal urine varies from 0·06 to 0·12%.

For the estimation of chlorine in blood, the proteins are coagulated by the addition of acetic acid and heating the mixture. After filtration, potassium alum and sodium carbonate are added, and the mixture is boiled and filtered, and the yellow filtrate is titrated with standard silver nitrate until a permanent red colour is obtained. W. G.

## General and Physical Chemistry.

**Determination of the Carrier in the Emission of the Continuous Spectrum by the Hydrogen Canal Rays.** J. Stark, M. Görcke, and M. Arndt (*Ann. Physik*, 1917, [iv], **54**, 81—110. Compare A., 1917, ii, 281).—The conditions under which the ultra-violet continuous spectrum is emitted by hydrogen canal rays have been investigated, and an attempt is made to identify the entities which are directly responsible for this radiation.

The intensity of the continuous spectrum increases as the wave-length diminishes from $\lambda$ 400 to $\lambda$ 240, and the increase is particularly marked in the region from $\lambda$ 280 to $\lambda$ 240. The distribution of the intensity is independent of the velocity of the hydrogen canal rays.

The continuous spectrum is emitted by the hydrogen canal rays in oxygen, and the intensity of this spectrum, as well as the distribution of the intensity, are the same as for the spectrum emitted by the canal rays in hydrogen. A continuous spectrum is also emitted by nitrogen canal rays in nitrogen and by oxygen canal rays in oxygen, but for cathode falls of potential varying from 800 to 8000 volts, the intensity of this spectrum is less than one-tenth of the intensity of the continuous spectrum emitted by the hydrogen canal rays. Nitrogen canal rays in hydrogen give rise to the emission of the hydrogen series lines in considerable intensity, but there is no appreciable continuous radiation even when the cathode fall of potential reaches 8500 volts.

From these observations, the conclusion is drawn that the emission of the continuous spectrum in question is characteristic of hydrogen. The facts suggest that the radiating entity is neither the hydrogen ion nor the neutral hydrogen atom, but that the continuous spectrum is due to an intermediate type in which the hydrogen ion is combined or associated with an electron, the combination representing a transition phase in the reversible change $H + \odot \rightleftharpoons H$.

H. M. D.

**Experimental Facts and Bohr's Theory of the Hydrogen Spectra.** J. Stark (*Ann. Physik*, 1917, [iv], **54**, 111—116).—A theoretical paper in which the author discusses recent observations on the continuous ultra-violet hydrogen spectrum in relation to Bohr's theory. The experimental evidence adduced in support of the view that the entities responsible for the emission of the continuous spectrum contain a single atom of hydrogen (compare preceding abstract) is considered to prove the untenability of Bohr's theory in its present form. Bohr's model of the hydrogen molecule is also incapable of affording an account of the facts which have led the author to the opinion that the many-lined spectrum is attributable to diatomic combinations carrying a single positive charge. H. M. D.

**Measurements in the Spectrum of Molybdenum according to International Normals.** MARTHA PUHLMANN (*Zeitsch. wiss. Photochem.*, 1917, **17**, 97—131).—Measurements of the wave-lengths of lines in the arc spectrum of molybdenum have been made with the aid of a large concave grating. The results obtained for the region λ 2420 to λ 4888 are recorded and compared with those given by Exner and Haschek. It has been suggested by Paulson that certain pairs of lines exhibit constant frequency differences, but the existence of this relation is not supported by the author's measurements. H. M. D.

**The Arc Spectrum of Tungsten according to International Units.** MARIA BELKE (*Zeitsch. wiss. Photochem.*, 1917, **17**, 132—142, 145—168).—Wave-length measurements of the lines in the arc spectrum of tungsten between λ 2249 and λ 6984 are recorded and compared with the results previously obtained by Exner and Haschek. The existence of pairs of lines with constant differences of frequency is not indicated by the measurements.
H. M. D.

**Colour of Inorganic Compounds.** F. RUSSELL VON BICHOWSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 500—508).—A theoretical paper in which an attempt is made to connect the colour of inorganic substances with the valence electrons and the stability of the electron grouping round the positive nucleus. H. M. D.

**The Polymorphism of certain Substances (Liquid Crystals and Sphaerolites with Helicoidal Winding).** PAUL GAUBERT (*Bull. Soc. franç. Min.*, **40**, 5; from *Chem. Zentr.*, 1917, ii, 806—807. Compare A., 1916, ii, 604; 1917, ii, 113).—Amyl cyanobenzylideneaminocinnamate has been found to exist in four different crystalline modifications. The stable α-form is biaxial, optically negative, and has a high rotatory power; it is obtained by crystallisation of the fused substance or by evaporation of solutions. The β- and γ-forms are sphærolitic and distinguished by differences in rotatory power; they are obtained by the rapid evaporation of solutions. The fourth modification is that described by Vorländer and Huth (A., 1911, ii, 165).

Anisylideneaminoazotoluene exists in five different crystalline forms, which are all biaxial. The stable α-form is monoclinic or triclinic, and the other four are probably rhombic. There are also two liquid anisotropic forms of this substance, one of which is optically positive and the other negative.

The cholesteryl esters of low freezing point readily form liquid crystals when their solutions are evaporated. A difference in the tendency to form solid crystals has been observed according to the optical character of the liquid phase. H. M. D.

**The Photolysis of Uranium Salts.** E. BAUER (*Schweiz. Chem. Zeit.*, 1918, **2**, 40—41).—When light is absorbed by a solution of a uranium salt, the uranyl ion undergoes a reversible change from the "dark" condition into the "light" condition; when the reverse action takes place, the light energy absorbed is given off again in the form of fluorescence. The addition of certain substances, such as chlorine or iodine ions, ferric and vanadyl salts, vanadic acid, and quadrivalent uranium salts, extinguishes the fluorescence. The same substances also destroy the Becquerel effect. In the "light" condition, the uranium is resolved into a higher (octavalent) and a lower (tervalent) stage of valency, and the two reunite to the sexavalent form in reverting to the "dark" condition. When an inhibiting substance is added, the formation of the intermediate products is prevented, because they are immediately taken up by the substance, for example, iodine to form the sexavalent ion. Under the influence of light, uranyl formate is decomposed with liberation of carbon dioxide and hydrogen, a reaction in which the octavalent uranyl ion plays a part. The reaction dies down again through the accumulation of the sexavalent ion, which acts as an extinguisher. Another instance of photolysis is the decomposition of oxalic acid by uranyl sulphate under the action of light. In this case, the octavalent intermediate ion produces carbon dioxide and the tervalent ion carbon monoxide, whilst the sexavalent ion is reconstituted. Analogous processes of simultaneous oxidation and reduction are held to account for the photosensitising effects of other fluorescent compounds, such as eosin. J. F. B.

**The Photolysis of Uranyl Formate.** E. C. HATT (*Zeitsch. physikal. Chem.*, 1918, **92**, 513—562).—The decomposition of solutions of uranyl formate under the influence of light has been further examined with a view to the determination of the influence of the concentration of the uranyl salt, the intensity of the light, and the presence of foreign substances.

The experiments with varying concentration indicate that the photolysis is retarded by the uranous salt, which is one of the products of the light reaction. For widely varying light intensities, the initial velocity of the reaction is proportional to the intensity of the light, but at later stages the velocity increases less rapidly than the intensity of the acting light. Potassium chloride, potassium iodide, ferric chloride, vanadyl sulphate, and vanadic acid retard the reaction, but potassium sulphite appears to produce no change in the velocity of the reaction. The view that uranium compounds of higher and lower valency are formed is rendered probable by the fact that the insolated solutions have an oxidising action on potassium iodide and a reducing action on potassium permanganate. In terms of the oxidation and reduction products, it is possible to explain a number of facts which have been established in this and previous investigations of the photochemical decomposition of uranyl formate (compare A., 1916, ii, 9).

A method for the estimation of uranous salts in presence of formic acid is described. The uranium solution acidified with sulphuric acid is added to a solution containing ammonium acetate and sodium phosphate placed in a cylindrical separating funnel connected below with a suction pump through a filter bottle. The funnel is provided with a Gooch filter and with an attachment by which the air in the funnel can be replaced by hydrogen. The mixture of uranyl ammonium phosphate and uranous phosphate, which is precipitated, is filtered by suction in the hydrogen atmosphere, the precipitate washed with ammonium acetate solution, and then dissolved in sulphuric acid (1:4), the solution thus obtained being titrated with standard permanganate. This method of estimating uranous salts has been found to give quite satisfactory results in the investigation of the insolated uranyl formate solutions. H. M. D.

**The Scattering of α-Rays as Evidence on the Parson Magneton Hypothesis.** David L. Webster (*J. Amer. Chem. Soc.*, 1918, **40**, 375—379).—The large-angle scattering of α-rays is generally considered to prove the untenability of theories of atomic structure which postulate large diffuse spheres of positive electricity. The magneton hypothesis, put forward by Parson (*Smithsonian Miscellaneous Collections*, 1915, **65**, No. 11), postulates such a structure, but the author contends that this is not really an essential feature, and that the α-ray scattering cannot be accepted as valid evidence against the magneton theory. H. M. D.

**Absorption Laws for Röntgen Rays.** R. Glocker (*Physikal. Zeitsch.*, 1918, **19**, 66—72).—This paper contains a discussion of the laws expressing the absorption coefficient of *X*-rays as a function of the wave-length and atomic number of the absorbing element, and contains tables of the various constants involved in the formulæ for ten elements and six compounds. The data are of practical and theoretical importance, but the paper cannot be suitably abstracted. F. S.

***X*-Ray Spectra and the Constitution of the Atom.** L. Vegard (*Phil. Mag.*, 1918, [vi], **35**, 293—326).—An account of work previously described (compare this vol., ii, 93, 94). The periodic variation of the electric conductivity of the elements (Benedicks, *Jahrb. Radioaktiv. Elektronik*, 1916, **13**, 362) is considered to afford support for the configurations which are put forward by the author. H. M. D.

**Solubility of Pure Radium Sulphate.** S. C. Lind, J. E. Underwood, and C. F. Whittemore (*J. Amer. Chem. Soc.*, 1918, **40**, 465—472).—If a solution containing a mixture of radium and barium salts is partly precipitated by the addition of a sulphate, the ratio of radium to barium in the precipitate is the same as in the original solution. The behaviour resembles that which is met with in the case of the isotopic elements, and has not yet been satisfactorily explained. With the object of providing data which may serve to elucidate the nature of the phenomenon, the authors have determined the solubility of pure radium sulphate in water and in sulphuric acid solutions.

The measurements were made by dissolving the salt and also by precipitating it from solution. The mean value obtained for the solubility in water at 25° is $2{\cdot}1 \times 10^{-8}$ gram per c.c., which is about one-hundredth of the solubility of barium sulphate. The presence of sulphuric acid up to 50% has no appreciable influence on the solubility. At higher acid concentrations, the solubility increases rapidly, the data obtained showing that the solubility is more than twelve times as great in 70% acid as in 60% acid. In dilute acid solutions, the solubility increases about 50% when the temperature is raised from 25° to 35°, and the same increase is found when the temperature is raised to 45°. The observed value of the solubility of radium sulphate is in agreement with that expected from a comparison of the solubilities of the sulphates of calcium, strontium, and barium.

The term pseudo-isotopy is given to the phenomenon which is exhibited by radium and barium sulphates. H. M. D.

**Radioactivity of the Lake of Rockange.** (Miss) H. J. Folmer and A. H. Blaauw (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 714—735).—A detailed account is given of the investigation of the radioactivity of samples of mud obtained by borings to different depths from the floor of the lake of Rockange (Hook of Holland). In contradiction to certain previous observations, the authors' results lead to the conclusion that the alluvial mud of the lake possesses no radioactivity of importance. The figures obtained correspond with an average value of the order of $10^{-12}$ gram of radium per gram. With regard to the origin of this, it is suggested that the radioactive substance in the mud is for the most part brought down by the rivers and does not come from the dunes. H. M. D.

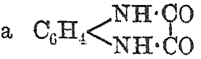
**Electrical Conductance of Solutions in Bromine.** Edward H. Darby (*J. Amer. Chem. Soc.*, 1918, **40**, 347—356).—Trimethylammonium chloride is readily soluble in liquid bromine, producing solutions of a yellow colour, the viscosity of which increases very rapidly with the concentration. The electrical conductivity of these solutions has been measured at 18° with results which show that the equivalent conductance of the salt increases from 0·3186 at $c = 0{\cdot}09076$ gram-equivalents per litre to 11·49 at $c = 1{\cdot}2356$. The variation of the conductance with the concentration is in agreement with the equation of Kraus and Bray. The constants have values which are comparable with those obtained for electrolytes in other solvents.

The conductance of trimethylammonium chloride is much greater than that obtained for iodine and phosphorus pentabromide, the conductance of which in liquid bromine has been previously examined by Plotnikov and Rokotjan (A., 1913, ii, 378).

H. M. D.

**The Influence of some Hydroxy-acids on the Electrical Conductivity of Boric Acid.** J. BÖESEKEN and H. KALSHOVEN (*Rec. trav. chim.*, 1918, **37**, 130—143).—In continuation of previous work (compare A., 1916, ii, 73, 209), the authors have examined the influence of glycollic, α-hydroxy-β-phenylpropionic, β-hydroxy-β-phenylpropionic, and diglycollic acids on the electrical conductivity of boric acid. Glycollic acid gave an increase in the conductivity, but the substitution of a group $\cdot O\cdot CH_2\cdot CO_2H$ for the hydroxyl group changed the influence from positive to negative, as shown by the results with diglycollic acid. β-Hydroxy-β-phenylpropionic acid is similar to β-hydroxybutyric acid (*loc. cit.*) in its influence. The influence of α-hydroxy-β-phenylpropionic acid is positive and almost equal to that of lactic acid (*loc. cit.*).

W. G.

**The Influence of some Derivatives of Nitrogen on the Electrical Conductivity of Boric Acid.** J. BÖESEKEN [with W. STURM and G. GOETTSCH] (*Rec. trav. chim.*, 1918, **37**, 144—161).—The nitrogenous compounds examined were carbamide, biuret, alloxan, alloxantin, glycine, glutamic, cyanuric, and dialuric acids, dihydroquinazoline (quinoxaline), and the glycol of uric acid. The results indicate that the presence of the group $\cdot NH\cdot CO\cdot$ has no influence on the electrical conductivity of boric acid, and that substances containing this group do not form complexes with boric acid. The results obtained with quinoxaline favour the ketonic formula  $C_6H_4{<}\begin{matrix}NH\cdot CO\\ |\\ NH\cdot CO\end{matrix}$ for this compound. Glycine forms a complex boric acid derivative, which is, however, dissociated to a large extent, judging from the slight increase in conductivity obtained. Alloxan in aqueous solution has $K < 5\times10^{-9}$, and it does not form a complex with boric acid. Dialuric acid does not form a complex with boric acid. It has $K = 6\times10^{-5}$, the value diminishing rapidly, probably owing to oxidation. Alloxantin dissociates in aqueous solution into dialuric acid and alloxan. The glycol of uric acid slightly increases the conductivity of boric acid.

W. G.

**The Influence of Boric Acid on the Electrical Conductivity of Diacetyl.** J. BÖESEKEN [with G. VAN DER HOEK OSTENDE] (*Rec. trav. chim.*, 1918, **37**, 162—164).—The results obtained, although incomplete, indicate that, in concentrated solution, diacetyl is dihydrated. It has an acid reaction in aqueous solution, having $K = \pm 4\times10^{-7}$.

W. G.

**The Influence of some Hydroxy-acids on the Electrical Conductivity of Boric Acid.** J. BÖESEKEN [with (MLLE.) J. WEISFELT, (MLLE.) J. VAN DER SPEK, CHR. VAN LOON, and G. GOETTSCH] (*Rec. trav. chim.*, 1918, **37**, 165—178. Compare preceding abstract).—Four acids were studied. α-Hydroxyoctoic acid, like other *α*-hydroxy-acids, gives with boric acid a complex having a high conductivity. Glyceric acid behaves like an *α*-hydroxy-acid, the *β*-hydroxyl group having no influence on the conductivity. Dihydroxymaleic acid behaves in aqueous solution like a di-*α*-hydroxy-acid. Its decomposition is retarded by boric acid. With gluconic acid, the increase in the conductivity is greater than that with the other *α*-hydroxy-acids, the group $\vdots C(OH)\cdot CO_2H$ exerting its influence in addition to that of the four other hydroxyl groups. The opening of the lactonic ring may be followed by the regular change in the conductivity, which increases with increase in the concentration of the hydrogen ions. W. G.

**The Influence of Boric Acid on the Conductivity of some Optically Active *α*-Hydroxy-acids, and on that of their Racemates.** J. BÖESEKEN and L. A. VAN DER ENT (*Rec. trav. chim.*, 1918, **37**, 179—183).—Measurements of the electrical conductivity of *r*- and *d*-amygdalic acids and *r*- and *d*-tartaric acids in the presence of boric acid show that the influence of a racemic acid on the electrical conductivity of boric acid is equal to that of its active component. W. G.

**Free Energy of Dilution of Sulphuric Acid.** MERLE RANDALL and O. E. CUSHMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 393—397).—The *E.M.F.* of cells of the type $H_2|H_2SO_4|Hg_2SO_4|Hg$ has been measured for widely varying sulphuric acid concentrations. From the results, the authors have calculated the free energy of the reaction $H_2+Hg_2SO_4=H_2SO_4+2Hg$ for acids of different concentration. In combination with previous data (compare A., 1914, ii, 521), these results also give the free energy of formation of sulphuric acid from 1*N* hydrogen and sulphate ions. The numbers obtained are tabulated. H. M. D.

**Electromotive Force and Free Energy of Dilution of Lithium Chloride in Aqueous and Alcoholic Solutions.** J. N. PEARCE and F. S. MORTIMER (*J. Amer. Chem. Soc.*, 1918, **40**, 509—523).—The influence of the solvent on the *E.M.F.* of concentration cells has been systematically examined in experiments with solutions of lithium chloride in water and the five lowest alcohols of the series beginning with methyl alcohol. The concentration ratio was in all cases 10 : 1, the absolute concentration of the stronger solution varying from 1·0 to 0·05 mol. of lithium chloride per litre.

The data recorded are those obtained with cells of two types. In the case of cells involving transference, the *E.M.F.* increases with increasing dilution in water and the three lower alcohols, but decreases with dilution in *n*-butyl and *iso*amyl alcohols. For cells arranged so that there is no transference, the observed *E.M.F.* decreases with increase in the dilution in all the solvents examined. These relations indicate that the ionisation of lithium chloride is abnormal in all these solvents.

The transport number of the lithium ion, the free energy of dilution, and the activity ratios for both the ions and the non-ionised molecules, have been calculated. The transport number increases with the dilution, whilst the free energy of dilution and the activity ratios decrease with the dilution in all the solvents examined.

An attempt is made to account for these relations by the assumption of effects due to hydration, polymerisation, and change in the dielectric capacity of the solvent. H. M. D.

**Effect of Interionic Force in Electrolytes. II.** S. R. Milner (*Phil. Mag.*, 1918, [vi], **35**, 352—364. Compare this vol., ii, 54). —The author's view, that the decrease in the molecular conductivity of electrolytes with increasing concentration is to be attributed mainly to a reduction in the mobilities of the ions, and not to a reduction in their number by their combination to form molecules, is discussed further by reference to the influence of interionic forces on the electrical conductivity and on the osmotic pressure. The theoretical investigation of this influence leads to the conclusion that a change in the concentration will produce identical variations in the conductivity and in the osmotic pressure of the free ions, that is to say, the ions which momentarily have no mutual energy with other ions.

This result, when applied to strong electrolytes, suggests that the observed changes in the conductivity and osmotic pressure of strong electrolytes with the concentration may be explained by a modification of the usual view. Interionic forces produce an increase in the frequency of occurrence of ions in an associated state, and the result of this is a reduction in the osmotic pressure of the free ions. The average mobility of an ion, taken over a period sufficiently long to include it in the free and associated state, is reduced in the same ratio, and the experimental facts are thus accounted for. If this view is correct, the ions of strong electrolytes are not associated into molecules, but pairs of oppositely charged ions which are temporarily in closest proximity will behave in a certain number of cases as if they were bound together.

H. M. D.

**Alternating Current Electrolysis with Mercury Electrodes.** Harry B. Weiser (*J. Physical Chem.*, 1918, **22**, 78—94). —When solutions of sodium thiosulphate are subjected to the action of an alternating current between metallic electrodes, metallic sulphides are precipitated in quantities which increase as the frequency of alternation decreases. The extent to which the electrodes are thereby corroded varies considerably with the nature of the electrode surface, and reproducible results cannot be obtained with solid metals.

When mercury electrodes are used, the changes in the surface tension give rise to a rhythmical vibration of the mercury surface which maintains the electrode in its original condition and serves to agitate the solution in the immediate neighbourhood of the electrode. In these circumstances, reproducible results are obtained, and experiments have been made in which the same frequency of alternation was used (72000 alternations per minute), but in which changes were made in the current density, the temperature, and the concentration of the sodium thiosulphate solution.

The corrosion of the mercury electrodes increases with the current density, but not in direct proportion. The departure from proportionality is greater in the more dilute solutions. The corrosion also increases with the concentration of the thiosulphate solution, the two quantities being approximately proportional. When the concentration reaches a certain limit, a film of sulphide is formed over the mercury surface, and this greatly reduces the corrosion. The corrosion increases with rise of temperature and is increased by mechanical stirring.

Under like conditions, zinc electrodes are corroded to a much smaller extent, and although it is probable that the above factors affect the degree of corrosion, as in the case of mercury, variations in the electrode surface have a much greater influence on the actual result. H. M. D.

**Thermal Leakage and Calorimeter Design.** WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 379—393).—The factors which play a part in the interchange of heat between a calorimeter and its environment are considered, more particularly with reference to the influence of the surrounding air. The convection currents in this air are of considerable importance in that the thermal leakage due to convection is approximately proportional to the square of the difference between the temperatures of the calorimeter and its environment. The influence of convection may be diminished by reducing the width of the air gap round the calorimeter. It is shown that gaps of from 10 to 17 mm. are most suitable for ordinary calorimeters, but larger gaps may be used in the case of large calorimeters in which smaller temperature differences are involved. Thin reflecting shields may be advantageously employed to diminish the effect of conduction.

H. M. D.

**Specific Heats at Low Temperatures of Sodium, Potassium, Magnesium, and Calcium Metals and of Lead Sulphide.** E. D. EASTMAN and W. H. RODEBUSH (*J. Amer. Chem. Soc.*, 1918, **40**, 489—500).—On the assumption that $C_v = 3R$ is the normal higher limit for the atomic heat of an element, it would seem that the strongly electropositive metals have exceptionally large atomic heat capacities, and in order to obtain further information on this point, measurements have been made of the specific heats of sodium, potassium, magnesium, and calcium between 65° and 300° (abs.).

The method used consisted in measuring the rise of temperature produced by a known quantity of electrical energy supplied to the metal suspended in a vacuum, the change of temperature being measured by means of a carefully calibrated copper–constantan thermocouple. From the values of $C_p$ derived from the experimental data, the values of $C_v$ were obtained by calculation according to methods previously described.

The results obtained show that the value of $C_v$ becomes considerably greater than $3R = 5{\cdot}97$ cal. over the higher portion of the range of temperatures examined. According to Lewis and Gibson (*J. Amer. Chem. Soc.*, 1917, **39**, 2554), the curve which is obtained by plotting $C_v$ against the logarithm of the absolute temperature is a general curve which can be made to fit the data for any one of a large number of elements by simple horizontal displacement. When the data obtained by the authors are examined in reference to this general curve, it is found that the points for sodium, magnesium, and calcium lie on the curve at lower temperatures, but are situated above it at the higher temperatures. In the case of potassium, the values of $C_v$ lie above the curve at all temperatures examined.

The deviations from the normal curve are considered to be due to the heat capacities of the electrons, the energy absorption of which is supposed to depend on the degree of constraint to which they are subjected in the atom. This constraint diminishes with increase in the electropositive character of the metal. H. M. D.

**Boundaries of Existence of the Liquid State.** W. HERZ (*Zeitsch. Elektrochem.*, 1918, **24**, 48—50).—The author has collected and tabulated the melting points and critical temperatures of a number of elements, halogen derivatives of non-metals, and some organic compounds. It is shown on comparison that in the case of metals the region of existence of the liquid decreases with increasing atomic weight in a given group of the periodic system, whilst for non-metals the region of existence increases. The same regularity holds for the halogen derivatives of the non-metals. In the case of organic compounds, the region of existence of the liquid increases with increasing molecular weight. The quotient, critical temperature/melting point, is approximately a constant for analogous groups of substances (see also Clarke, *Amer. Chem. J.*, 1896, **18**, 618). J. F. S.

**The Cryoscopic Constant of Asymmetric Heptachloropropane, $CCl_3{\cdot}CCl_2{\cdot}CHCl_2$.** J. BÖESEKEN and J. BENEDICTUS (*Rec. trav. chim.*, 1918, **37**, 121—129).—Determinations have been made with a large number of different substances, and the results show that the heptachloropropane has a cryoscopic constant just under 120, but the solubility in it of hydroxy-compounds and acids is not very great. Acids are strongly associated in this solvent, even acids of high molecular weight, giving values equal to twice the theoretical molecular weight. Alcohols at great dilutions give almost normal molecular weights, but as the concentration increases they become associated. Hydrocarbons, chloro-compounds, amines, and esters behave normally. W. G.

**Formula giving the Saturated Vapour Pressure of a Diatomic Liquid.** E. ARIÈS (*Compt. rend.*, 1918, **166**, 447—450. Compare this vol., ii, 61).—The author deduces the formula $\Pi=\tau^{11/4}Z/x$, where $x=[1+\{(1-\tau)(0\cdot86-\tau)\}/(0\cdot353\tau^2+0\cdot642)]\tau^{\frac{7}{4}}$, and shows that the calculated results agree with the observed results in the cases of chlorine and carbon monoxide. W. G.

**The Anomalies which the Saturated Vapour Pressures of certain Diatomic Liquids Show.** E. ARIÈS (*Compt. rend.*, 1918, **166**, 553—556).—The formula previously deduced from a study of chlorine and carbon monoxide (preceding abstract) applies also to hydrogen chloride and hydrogen iodide, but in the cases of oxygen, nitrogen, and nitric oxide certain anomalies occur between the values as calculated and observed. W. G.

**Thickness and Structure of the Capillary Layer of a Liquid in Contact with its Saturated Vapour.** G. BAKKER (*Ann. Physik*, 1917, [iv], **54**, 245—295).—By making use of the Laplacian theory of capillarity and certain thermodynamic arguments, it is shown that the number of molecules in the surface layer increases from about three at the freezing point of the liquid to a very much larger number in the neighbourhood of the critical temperature. In the case of carbon dioxide at the reduced temperature 0·999°, the number obtained lies between 300 and 1800. Thermodynamic reasoning leads to the conclusion that the thickness of the surface layer is about 1·5 $\mu\mu$ at the reduced temperature 0·9°, whilst in the immediate neighbourhood of the critical temperature the thickness increases to a value represented approximately by half the wave-length of violet light. The thermodynamic method gives results which agree with those previously mentioned in so far as the number of molecules in the surface layer is concerned.

Since the number of molecules in the surface layer is very limited if the temperature is not in the neighbourhood of the critical temperature, it follows that the radius of action of the attractive forces does not extend beyond the limits of the nearest molecules. This deduction is not compatible with the assumptions involved in the original theory of Laplace. H. M. D.

**The Law of Thermochemical Processes (Summary) and of Photochemical Processes.** MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1918, **102**, 81—129).—According to the author's theory, reactions in gases take place only between molecules which are in an "activated" condition. A species of thermal isomerism of the molecule is assumed, and the heat energy necessary to transform the inactive into the active modification is termed the "heat of activation." In the mass-action equations developed from thermodynamic principles for reactions of the first and second orders, the factor representing the heat of activation appears as an exponential function, and from two determinations of the velocity constant of a reaction at two different temperatures, it is possible to calculate the heat of activation. The heat of activation is a fraction of the total heat of decomposition into atoms, and this fraction can be calculated from the heat of reaction and the heat of activation. In the case of the reaction $H_2 + I_2 \rightleftharpoons 2HI$, for instance, the fraction is between one-fourth and one-third.

According to the author's theory, the time of contact between two "activated" molecules is of so short duration that the chance of simultaneous contact with a third activated atom is very small indeed. Reactions of a higher order than the second are therefore held to be impossible (compare A., 1915, ii, 338, 623, 828; 1916, ii, 304, 422).

The theory is applied to photochemical reactions, and equations are given for reactions of the first and second orders. The relation of the heat of activation to the frequency of the actinic radiation is considered, with special reference to Planck's radiation law, which is deduced in a novel manner. Just as the course of a thermochemical reaction is determined by the smallest heat of activation, to the exclusion of those reactions requiring greater heats of activation, so a photochemical reaction is determined by the smallest radiation frequency to which the substance is resonant. The relation between heat of activation and radiation frequency is expressed by an equation $q = R\beta v$, where $q$ is the heat of activation and $v$ is the frequency proper to the reaction. This frequency should be found in the spectrum of the reacting substances, and the possibility arises of determining heats of reaction and heats of activation spectroscopically. The theory is examined in its relation to Bunsen and Roscoe's law and the law of photochemical equivalents. E. H. R.

**The Energy Theory of Matter.** H. STANLEY REDGROVE (*Chem. News*, 1918, **117**, 145—146. Compare A., 1917, ii, 411).—In a recent paper (A., 1917, ii, 164), Thornton pointed out that a constant is obtained if the molecular heats of combustion of saturated hydrocarbons are divided by the corresponding numbers of oxygen atoms which are required for the complete combustion of the hydrocarbons. An attempt has been made (Vliet, this vol., ii, 98) to utilise this relation in the calculation of the contribution of the carbon and hydrogen atoms and the valency bonds towards the heats of combustion of their compounds. It is shown that the equation thus introduced is deducible from the equations given by the author, and thus affords no additional basis for the calculations in question.

The author criticises the significance of the relation indicated by Thornton, and contends that it is not generally applicable to different groups of organic compounds.

The advantages of the author's theory as a basis for the computation of additive or partly additive properties are discussed in relation to other underlying hypotheses. H. M. D.

**Equilibria Involving Cyanogen Iodide. The Free Energy of Formation of Cyanogen.** GILBERT N. LEWIS and DONALD B. KEYES (*J. Amer. Chem. Soc.*, 1918, **40**, 472—478).—The reversible reactions represented by $2CNI \rightleftharpoons (CN)_2 + I_2$ and $CNI + HI \rightleftharpoons HCN + I_2$ have been examined, and from the equilibrium data the free energy of formation of cyanogen has been calculated.

The partial pressure of iodine in the saturated cyanogen iodide vapour was determined colorimetrically by comparison of this with the vapour given off by pure solid iodine, the temperature of which was adjusted until the colours in the two comparison tubes were equal. The partial pressure obtained in this way increases from 3·42 mm. at 90·0° to 56·7 mm. at 123·0°. From these partial pressures, the equilibrium constant is calculated, and the logarithms of these numbers when plotted against the reciprocal of the absolute temperature fall very nearly on a straight line, from the slope of which the heat absorbed in the dissociation is found to be 48,000 cal. By extrapolation, the value of the equilibrium constant at 25° is obtained, and this leads to $\Delta F_{298} = 14{,}950$ for the free energy of the reaction represented by $2CNI(\text{solid}) = (CN_2) + I_2(\text{gas})$.

When a mixture of solid cyanogen iodide and iodine is treated with a dilute solution of hydriodic acid, the equilibrium represented by $CNI + H^{\cdot} + I' \rightleftharpoons HCN + I_2$ is quickly established, and methods are described by which the authors have found it possible to obtain the concentrations of the hydrogen and iodine ions and that of the hydrocyanic acid for a series of hydriodic acid solutions of varying strength. The values obtained for $K = [HCN]/[H^{\cdot}][I']$ are not very constant, but by taking the mean value $K = 13$, the free energy of the reaction $CNI(\text{solid}) + H^{\cdot} + I' = HCN(\text{gas}) + I_2(\text{solid})$ is found to be $\Delta F_{298} = -1520$.

Measurements of the partial pressure of hydrogen cyanide for aqueous solutions of varying concentration gave $P/m = 0{\cdot}096$ at 25°, where $P$ is the pressure in atmospheres and $m$ the concentration in mols. per 1000 grams of water. From this ratio of distribution, the value $\Delta F_{298} = 1390$ is obtained for the reaction $HCN(\text{aq.}) = HCN(\text{gas})$. By combining these with values previously obtained, the free energy of formation of cyanogen iodide according to the equation $C(\text{gas}) + \frac{1}{2}N_2 + I(\text{solid}) = CNI(\text{solid})$ is found to be $\Delta F_{298} = 38{,}635$.

Combining this result with the equations for the free energy of dissociation of cyanogen iodide (see above) and the formation of iodine vapour from solid iodine, the free energy of formation of cyanogen gas according to the equation $2C(\text{gas}) + N_2 = (CN)_2(\text{gas})$ is found to be $\Delta F_{298} = 87{,}580$. H. M. D.

**The Oxidising Power of Cyanates and the Free Energy of Formation of Cyanides.** GILBERT N. LEWIS and THOMAS B. BRIGHTON (*J. Amer. Chem. Soc.*, 1918, **40**, 482—489).—The experiments described were undertaken with the object of providing data for the calculation of the free energy of formation of hydrogen cyanide, a substance which is of considerable importance in connexion with the determination of the free energy changes associated with many different types of organic reactions.

Fused potassium cyanide is oxidised by carbon dioxide, and the fused cyanate is reduced by carbon monoxide. The equilibrium condition resulting from these opposed reactions has been examined by determining the value of $K=[CO_2]/[CO]$ for the gas mixture in equilibrium with the eutectic mixture of potassium cyanide and potassium cyanate at various temperatures between 721° and 847° (abs.). Preliminary experiments showed that the eutectic temperature is 555° (abs.), and that the mixture contains 14·6% of potassium cyanide. When the values of $K$ are plotted against $1/T$, a straight line is obtained, and by extrapolation to the temperature of the eutectic point this gives $K=0·89$. From this value of $K$, the free energy of the reaction $KCNO(solid)+CO(gas)=KCN(solid)+CO_2(gas)$ is found to be $\Delta F_{555}=126$. This, in combination with the value for the heat of the reaction at the ordinary temperature $\Delta H=4300$ cal., gives $\Delta F_{298}=2060$ for the free energy of the reaction at 25°.

From solubility and freezing-point data, the free energy change associated with the conversion of the solid salts into the corresponding ions in normal concentration has been found to be $\Delta F_{298}=-2130$ for potassium cyanide and $\Delta F_{298}=-1440$ for potassium cyanate. By combination of these results with the previous one, the free energy of the change $CNO'+CO(gas)=CN'+CO_2(gas)$ is found to be $\Delta F_{298}=1370$.

From this and free energy values previously derived, it follows that for the reaction $C(gas)+\frac{1}{2}N_2+\odot=CN'$, $\Delta F_{298}=35{,}277$, and since the free energy of formation of the hydrogen ion is taken as zero, we have for $\frac{1}{2}H_2+C(gas)+\frac{1}{2}N_2=H^{\cdot}+CN'$, $\Delta F_{298}=35{,}277$. This result, in combination with $\Delta F_{298}=11{,}856$ for the free energy of the reaction $HCN(aq.)=H^{\cdot}+CN'$, gives for the free energy of formation of hydrogen cyanide in accordance with the equation $\frac{1}{2}H_2+C(gas)+\frac{1}{2}N_2=HCN(aq.)$ the value $\Delta F_{298}=23{,}421$.

H. M. D.

**Gas Dilatometer for ascertaining Decomposition Points.** W. C. Moore and J. B. Davies (*Met. and Chem. Eng.*, 1918, **18**, 301—304).—The substance examined is heated in a vacuous glass test-tube placed vertically in a paraffin bath. Distillation products pass into a horizontal pipette-shaped air condenser sealed on to the test-tube and closed at the other end by a U-shaped manometer filled with mercury. The pressure in the apparatus is plotted as the temperature rises. A discontinuity in the curve due to the rapid evolution of permanent gas is taken as the decomposition point. The results are influenced by rate of heating, but when this was 1° per minute up to 150° and then slower, the following results were obtained: sucrose 178°, dextrose 177°, and soluble starch 214°, whilst with cellulose (filter paper) a slow decomposition commenced at 143°, with further points at 185° and 204°.

H. J. H.

**Compressibility and Dilatability of Gases.** A. LEDUC (*Ann. Physique*, 1918, [ix], **9**, 5—28).—A detailed description of a piezometer which can be used to observe the gases successively at pressures of 1, 2·8, and 5 atmos., which has been used for neon and argon. The following are the values of the constants found for neon: coefficient of departure from Mariotte's law, $-6{\cdot}10^{-6}$ per cm. of mercury at 17° between 1 and 5 atmos.; molecular volume at 0° and 760 mm., 1·0004; atomic weight, 20·15; coefficient of dilatation, $\beta = 3664 . 10^{-6}$ between 5° and 30°. For argon the values are: coefficient of departure from Mariotte's law, $10{\cdot}2 . 10^{-6}$ between 1 and 5 atmos.; molecular volume, 0·9990 at 0° and 760 mm.; atomic weight, $39{\cdot}91 \pm 0{\cdot}01$; coefficient of dilatation, $\beta = 3669 . 10^{-6}$ between 8° and 32°. W. G.

**Fluidity and Specific Volume of Aqueous Solutions.** W. HERZ (*Zeitsch. anorg. Chem.*, 1918, **102**, 173—176. Compare A., 1917, ii, 361).—Curves are given showing that, for aqueous solutions of a number of acids, for example, sulphuric and acetic, alkalis such as sodium and potassium hydroxides, hydrolysed salts. such as sodium carbonate and ferric chloride, and neutral substances such as sucrose, there is a direct proportionality between the fluidity expressed in *C.G.S.* units and the specific volume. Even in the case of mixed solutions, for example, a solution containing sodium and copper sulphates, the proportionality holds. E. H. R.

**Soap Solutions. III.** VICTOR LENHER and GEORGE H. BISHOP (*J. Physical Chem.*, 1918, **22**, 95—98).—The adsorption of sodium oleate by Ceylon graphite, willow charcoal, and animal charcoal has been examined by filtering a *N*/10-solution through 30 cm. columns of the principal materials. Successive fractions of the filtered liquid were analysed, and the process continued until no further adsorption occurred. The results show that animal charcoal has a much greater adsorbent capacity than wood charcoal, which, in turn, adsorbs sodium oleate more readily than graphite. H. M. D.

**Theory of Dyeing.** H. R. KRUYT and (MISS) J. E. H. VAN DER MADE (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 636—641).—The observations recorded by Reinders (A., 1913, ii, 836) have led the authors to investigate further the influence of various salts on the distribution of dyes between water and *iso*butyl alcohol.

Experiments made with crystal-violet, magenta and methylene-blue, and the sodium salts of different acids show that the sequence of the anions, when arranged according to their influence on the distribution of the basic dye, is identical with the lyotropic series. This sequence is no longer found when acid dyes are substituted for the basic dyes.

The influence of salts on the adsorption of dyes by blood charcoal has also been examined. In the case of methylene-blue-B extra and auramine-O, the order is not that of the lyotropic series, and it is supposed that the electrical charges of the ions have a preponderating influence. With crystal-violet, on the other hand, the sequence of the sodium salts is that of the lyotropic series. [See, further, *Ind.*, 238A.] H. M. D.

**A New Method for the Measurement of the Coefficient of Diffusion of Electrolytes.** St. Procopiu (*Ann. Physique*, 1918, [ix], **9**, 96—112).—In a broad, vertical tube are superposed two layers of different concentration of the same electrolyte, and the variation of a physical or chemical property, at a given distance from the surface of contact with the time is estimated. In this case, the *E.M.F.* between an electrode of the metal contained in the electrolyte and a similar electrode at a much greater distance is studied, and the time taken for it to reach its maximum is determined. Then $D=x^2/2\theta$, where $D$ is the coefficient of diffusion, $x$ is the distance of the first electrode from the surface of contact, and $\theta$ is the time taken for the *E.M.F.*, and consequently the concentration at $x$, to attain its maximum. W. G.

**Experiments on the Manifestation of Osmotic Pressure with Membranes of Chemically Inert Materials.** S. L. Bigelow and C. S. Robinson (*J. Physical Chem.*, 1918, **22**, 99—127).—The experiments described were made with the object of ascertaining whether osmotic effects are exhibited under conditions which seem to preclude the possibility of chemical reaction between the membrane and the solvent. For this purpose, membranes were constructed from silica, graphite, amorphous carbon, copper, silver, and gold in a very finely divided state. These materials were compressed into the form of disks, which served to separate the solvent and solution. A special type of osmotic cell was devised which appeared to be adapted to the use of membranes of this type.

Preliminary results obtained for sucrose solutions (0·5 to 2 molar) are recorded which show that small osmotic effects are exhibited with these chemically inert membranes. By varying the degree of compression of the disks, the diameter of the pores could be altered, and it has been found that such variations are accompanied by a change in the osmotic effect in the sense that this increases with diminution in the size of the pores.

With copper membranes, negative osmotic effects have been observed. Similar results have been previously recorded for kaolin membranes. H. M. D.

**Crystal Structure of the Alums and the Rôle of the Water of Crystallisation.** L. Vegard and H. Schjelderup (*Ann. Physik*, 1917, [ii], **54**, 146—164).—Bragg's method has been applied in the investigation of the crystal structure of the alums by observations on crystals of potassium alum, ammonium alum, iron ammonium alum, and chrome alum. Using the rhodium line

$\lambda = 0{\cdot}607 \times 16^{-8}$ cm., the authors measured the relative intensities of the spectra of different orders obtained by reflection from the (100), (110), and (111) planes, and from the results have deduced the probable arrangement of the metal, sulphur, and oxygen atoms in the space-lattice system. For a description of the rather complicated structure, the original paper must be consulted.

The crystal model divides the twenty-four molecules of water into six groups, which groups are cubically disposed with reference to the four tetrahedrally arranged atoms of sulphur. The model makes no distinction between the water of crystallisation and the other constituents of the alum. Any hypothesis which would distinguish the water of crystallisation from water of constitution could not be reconciled with the observed relations between the high-frequency reflection spectra. The removal of the water of crystallisation is necessarily accompanied by the destruction of that structure which is characteristic of the hydrated salt.

The zeolites obviously present an attractive material for investigation in regard to the influence of the water content on the crystalline structure, and observations of a preliminary character have been made on chabasite, crystals of which were dehydrated by heating at 200—300°, and examined before and after dehydration by the *X*-ray method. The results show that the relative intensities of the spectra of different orders are not appreciably altered by the loss of water. The dehydration is, however, accompanied by a diminution in the absolute intensities, and more particularly by a decrease in the sharpness of the maxima.

The assumption that the water molecules do not form an essential part of the space lattice of the zeolite is held to be inadmissible. The facts can be accounted for by the hypothesis that the weakened reflection of the partly dehydrated crystals is due to crystal elements which have not lost water, and retain therefore their original configuration. Crystal elements which have lost water and from which new structures have been formed are presumably orientated in all possible directions, and for this reason play a minor part in the effective reflection of the *X*-rays.

H. M. D.

**In-, Uni- and Bi-variant Equilibria. XVIII.** F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 659—667. Compare A., 1917, ii, 454).—A further discussion of the equilibrium relations in systems of *n*-components with *n*-phases at constant temperature with varying pressure. The properties of such systems are very similar to those which have already been described for conditions in which the pressure is constant and the temperature variable. H. M. D.

**One-sided Chemical Equilibria.** E. Baur (*Schweiz. Chem. Zeit.*, 1918, ii, 25—26).—When salicylic acid is heated at 200°, it volatilises, and the vapour undergoes partial dissociation into phenol and carbon dioxide. The degree of dissociation is dependent on the pressure and follows the law of mass action, $P \cdot a^2/1 - a^2 = K = 254 \cdot 9$, where $P$ is the pressure in cm. of mercury and $a$ is the measured degree of dissociation. Although the dissociation is correctly described as an equilibrium, yet no synthesis of salicylic acid from phenol and carbon dioxide can take place in the gaseous condition. Hence the reaction, being irreversible, is a "one-sided" equilibrium. Another instance of a similar phenomenon has been observed in the formation and decomposition of phloroglucinolcarboxylic acid. Phloroglucinol and potassium hydrogen carbonate in aqueous solution give a partial formation of potassium phloroglucinolcarboxylate. At 50°, the equilibrium is adjustable from both sides and follows the law of mass action. When the velocity of the changes, on the one hand the formation and on the other the decomposition, of the carboxylate is studied in solutions saturated with phloroglucinol, it is found that for the expression $V = K(C - C_1)$, where $C$ is the momentary and $C_1$ the equilibrium concentration of the carboxylate, the value of $K$ is about one-fourth in the formation of its value in the decomposition. This is explained on the ground that the decomposition of the carboxylate may take place in two ways, directly and by way of an intermediate ester salt, potassium phloroglucinol carbonate, whereas the formation of the carboxylate can only take place in one way, namely, through this intermediate stage. If this way through the ester salt did not exist, the carboxylate could decompose, but not re-form, yet the limit of the decomposition must be the same as it actually is where both ways are available. J. F. B.

**Reversible Reactions of Sulphur Compounds.** GILBERT N. LEWIS, MERLE RANDALL, and F. RUSSELL VON BICHOWSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 356—362).—An account is given of preliminary experiments which were undertaken with the object of finding reversible reactions suitable for the investigation of the free energy changes of sulphur compounds.

Towards aqueous solutions of various salts, sulphur begins to exhibit considerable reactivity when the mixtures are heated at 150° to 200°. Mercuric, ferric, and stannic salts are quantitatively reduced, and mercurous, cupric, bismuth, and lead salts are slowly but quantitatively precipitated as sulphides. Nitrate, permanganate, iodate, and bromate ions are reduced to nitric oxide, manganese dioxide, iodine, and bromine respectively. Chlorates appear to be reduced very slowly, but sulphates, periodates, and perchlorates are not acted on at 180°. The reactions in question are probably due to the reversible change $2H_2O + 3S = 2H_2S + SO_2$, the sulphur dioxide being the active reducing agent.

Solid sulphates are reduced by hydrogen at moderate temperatures, and the sulphate ion is reducible at about 150° by mild reducing agents.

The investigation of the decomposition of silver sulphite on heating shows that the reaction does not occur in accordance with the equation $Ag_2SO_3 = Ag_2O + SO_2$, but that the solid product of the reaction is either a basic salt or a solid solution. In presence of water, reaction takes place more rapidly in accordance with the equation $2Ag_2SO_3 = 2Ag + Ag_2SO_4 + SO_2$, this reaction being catalysed by the water. Sulphuric acid is then produced in consequence of the further reaction represented by $Ag_2SO_4 + SO_2 + 2H_2O = 2Ag + 2H_2SO_4$.

The potential of the sulphur dioxide electrode has also been examined by measuring the *E.M.F.* of the cell $Pt|SO_2|H_2SO_4|Hg_2SO_4|Hg$ for varying concentrations of the sulphuric acid and varying partial pressures of the sulphur dioxide. It has not been possible to find a satisfactory interpretation of the results obtained.

H. M. D.

**Equilibrium in the Reaction between Water and Sulphur at the Boiling Point of Sulphur.** Gilbert N. Lewis and Merle Randall (*J. Amer. Chem. Soc.*, 1918, **40**, 362—367).—The equilibrium in the system $2H_2O + 3S = 2H_2S + SO_2$ has been examined at the boiling point of sulphur. The experiments were made in the presence of an excess of sulphur, and in these circumstances the partial pressure of this compound was constant. A weighed quantity of water, enclosed in a thin-walled sealed tube, was introduced into the reaction chamber, consisting of a glass bulb of known capacity, which was heated in the vapour of boiling sulphur. The formation of hydrogen sulphide and sulphur dioxide is accompanied by an increase in the pressure when the volume of the reaction mixture is kept constant, and the pressures required to maintain this condition were measured in a series of experiments in which varying quantities of water were introduced into the reaction bulb. From these pressures, it is possible to calculate the partial pressures of the hydrogen sulphide, sulphur dioxide, and water in the reacting mixture.

Some difficulties were met with by reason of the fact that the water adsorbed by the surface of the glass is partly given off at the temperature of the experiments, but suitable allowance was made for the effect thereby produced.

The results obtained in six experiments gave values of $K = [H_2S]^2[SO_2]/[H_2O]^2$ varying from 0·00088 to 0·00232. The differences between these results are not considered excessive when the multiplication of errors, which the formula involves, is taken into account. The mean value $K = 0{\cdot}00154$ may be used in the calculation of the free energy of formation of sulphur dioxide.

H. M. D.

**Equilibrium in the Reaction between Water and Sulphur at High Temperatures. The Dissociation of Hydrogen Sulphide.** Merle Randall and F. Russell von Bichowsky (*J. Amer. Chem. Soc.*, 1918, **40**, 368—375. Compare preceding abstract).—The equilibrium in question has been further investigated at higher temperatures, where free hydrogen is formed by the dissociation of the hydrogen sulphide. The equilibrium mixture contains, therefore, the five gases, water, sulphur, hydrogen sulphide, sulphur dioxide, and hydrogen. If the dissociation constant of hydrogen sulphide is known, the composition of the equilibrium mixture of the five gases can be calculated if the original composition of the mixture, the total pressure, and the partial pressure of one of the five gases are determined.

The partial pressure of the hydrogen has been measured by the use of an evacuated platinum bulb inserted into the reaction chamber, into which the hydrogen diffused until the pressure in the bulb became equal to the partial pressure of the hydrogen in the gas mixture. This apparatus was used in the extension of previous measurements of the dissociation of hydrogen sulphide to higher temperatures. The values obtained for $K_p=[H_2S]/[H_2][S_2]^{\frac{1}{2}}$ when the pressures are measured in atmospheres decrease from 7·98 at 1362° (abs.) to 1·81 at 1667° (abs.). These results agree with the observations of Preuner and Schupp (A., 1909, ii, 977), whose measurements extended to 1405° (abs.).

In the investigation of the more complex equilibrium, a mixture of gases of known composition was obtained by electrolysing a 10% solution of potassium hydroxide in two separate vessels, the oxygen from one or both of which could be passed over boiling sulphur and converted into sulphur dioxide. The currents passing through the electrolysers, which were placed in parallel, were accurately measured and afforded the data for the calculation of the composition of the original mixture. Since the experiments were made at atmospheric pressure, the further quantity required was readily obtained.

The results obtained in experiments at temperatures ranging from 1160° (abs.) to 1645° (abs.) are used in the calculation of the logarithm of the equilibrium constant $K_p=[H_2O]^2[H_2S]/[H_2]^3[SO_2]$, corresponding with the equation $3H_2+SO_2=2H_2O+H_2S$. The value of $\log K_1$ (partial pressures being measured in atmospheres) decreases from 5·93 at 1160° to 2·56 at 1645° (abs.).

H. M. D.

**Studies in Esterification. X. The Esterification of Benzoic and the Toluic Acids by Methyl, Ethyl, and Propyl Alcohols.** RAYMOND FREAS and E. EMMET REID (*J. Amer. Chem. Soc.*, 1918, **40**, 569—578).—A re-examination of the position of equilibrium attained by various mixtures of methyl, ethyl, or propyl alcohol with benzoic or one of the toluic acids, or by mixtures of the esters with water. The binary mixture, of known composition, was in each case sealed in a glass tube and heated for four or eight days at 200°, the proportion of acid in the final mixture being then estimated and the percentage of equivalent amounts esterified or hydrolysed at equilibrium calculated by the formula given by Faber and Reid (A., 1917, i, 626). Under these conditions, it is found that with mixtures of any pair of the above alcohols and acids, or of one of the esters with water, in varying proportions, the position of equilibrium accords closely, although not exactly, with the law of mass action, this result agreeing with that of Berthelot and Pean de St. Gilles. Of the toluic acids, the ortho-compound shows the least and the para-compound the highest esterification limit towards methyl alcohol, but the reverse is true of the esterification limits towards ethyl and propyl alcohols; the esterification limit of any one of the four acids is lower towards ethyl alcohol than towards propyl or methyl alcohol, the latter giving the highest value with each of the acids. D. F. T.

**The Hydrolysis of Methyl Sulphate and Ethyl Sulphate with Sodium Methoxide or Ethoxide.** J. POLLAK and A. BAAR (*Monatsh.*, 1918, **38**, 501—523).—Methyl sulphate undergoes hydrolysis by water more rapidly than ethyl sulphate (Claesson, A., 1879, 775; Kremann, A., 1907, ii, 241), but in the presence of potassium hydroxide the ratio of the reaction velocities is very different from that observed for the hydrolysis by water only. With 0·5*N*-potassium hydroxide at 25°, the unimolecular constant for methyl sulphate is forty-five times as great as for the ethyl ester, whereas with water only the ratio is approximately 5:1. In order to decide whether the difference is due to the difference in the solubility of the two esters in water, and to avoid the possibility of such a disturbing factor, it is desirable to examine the rate of reaction in a homogeneous system. Kremann (A., 1907, ii, 157) has already observed that with methyl and ethyl alcohol, the rate of reaction of methyl sulphate is three to four times that of ethyl sulphate. With an alcoholic solution of sodium ethoxide, however, at 25° methyl sulphate reacts approximately twenty-five times as rapidly as ethyl sulphate, whilst at 0° the ratio is 58:1. The reaction in each case proceeds as far as the corresponding alkyl hydrogen sulphate or its sodium salt, any further hydrolysis being negligible. These results demonstrate that the great difference in the velocities of reaction of alkali on the two alkyl sulphates is not mainly due to any difference of solubility on the part of the sulphates, because a similar difference is observed in homogeneous and in heterogeneous systems. The difference is therefore presumably to be attributed to the different character of the reactions, the alkali hydrolysis yielding the alkali salt of the alkyl hydrogen sulphate, whilst the free alkyl hydrogen sulphate is produced by the action of water or of alcohol.

Examination of the reaction velocity of ethyl and methyl sulphates with alcohol in the presence of a gradually increasing proportion of water shows that the former ester is distinctly less soluble in water, and that the difference in the solubility of the two esters may exert an appreciable influence on the relative apparent reactivity of the two esters towards alkali hydroxide in the heterogeneous aqueous system. Methyl alcohol reacts with the two alkyl sulphates more rapidly than does ethyl alcohol, and although it was found that, as expected, sodium methoxide affects the methyl ester much more rapidly than the ethyl ester, the surprising result was obtained that sodium methoxide in methyl-alcoholic solution is less reactive than an ethyl-alcoholic solution of sodium ethoxide. A similar observation to this has already been made in certain cases, for example, by Lobry de Bruyn and Steger (A., 1899, i, 745, 849), Steger (A., 1889, i, 745), and Kremann (A., 1905, ii, 307), but the suggestion of the last-named, that the difference is due to the presence of traces of water which cause a greater proportion of hydrolysis in the sodium ethoxide, is discredited, and the suggestion is made that the explanation may be found in the possible occurrence of the reaction between the alkyl sulphate and the undissociated portion of the sodium alkoxide (compare Wegscheider and Amann, A., 1915, ii, 757). D. F. T.

**The Velocity of Formation of Nitrosyl Bromide, $2NO + Br_2 = 2NOBr$.** MAX TRAUTZ and VASANJI P. DALAL (*Zeitsch. anorg. Chem.*, 1918, **102**, 149—172. Compare A., 1916, ii, 304, and this vol., ii, 151).—The investigation of this reaction was limited to temperatures between $-15°$ and $+15°$, to bromine pressures of 11—26 mm., and nitric oxide pressures of 11—12 mm. At greater temperatures or pressures, nitrosyl bromide decomposes, and at lower temperatures the bromine condenses on the glass of the vessel. In presence of excess of bromine, the reaction appears to be of the third order, the velocity constants found lying between $0{\cdot}9$ and $1{\cdot}6 . 10^{10}$. Probably, however, there are two superimposed reactions, the first, $NO + Br_2 \rightleftharpoons NOBr_2$, coming to equilibrium very quickly, whilst the second, $NOBr_2 + NO \rightleftharpoons 2NOBr$, is measurable. The temperature coefficient is very small, apparently slightly greater than unity, and could not be determined with certainty. On the supposition that the reaction takes place in the above two stages, the "heat of activation" is calculated, and is found to be 3076 cal. The velocity constants calculated from this number agree substantially with the observed values and support the authors' theory of thermochemical processes. E. H. R.

**Velocity of Dissolution of the Metals in Acids. III. Velocity of Dissolution of Alloys of Zinc with Arsenic, Lead, Cadmium, Nickel, Platinum, and Gold.** M. CENTNERSZWER (*Zeitsch. physikal. Chem.*, 1918, **92**, 563—580. Compare A., 1914, ii, 550; 1915, ii, 158).—The observations previously made on the rate at which hydrogen is evolved from solutions of hydrochloric acid by zinc–copper alloys have been extended to alloys of zinc with other metals. The results obtained show that arsenic, lead, and cadmium produce no increase in the rate of dissolution of the zinc. The contrary observations recorded by previous observers are attributed to the presence of traces of other metals—probably iron or copper. The facts established by the author's experiments are difficult to reconcile with the theory of local elements.

Very small quantities of nickel, platinum, and gold of the order of 0·01% produce an appreciable increase in the rate of dissolution of zinc.

The results obtained lead to the conclusion that pure zinc is not acted on by either hydrochloric or sulphuric acid if the concentration is less than about 0·5 to 1$N$. H. M. D.

**Method for the Carrying Out of Catalytic Reactions.** JOHANN WALTER (D.R.-P., 295507; from *Chem. Zentr.*, 1917, i, 291).—Thorough exposure of the catalyst to the reagents is achieved by electromagnetic means. The catalyst itself may be magnetic and if desired spread on a non-magnetic material, or a non-magnetic catalyst may be deposited on a magnetic substance, and parts of the apparatus, such as baffle plates or gauze in a gas tube, or mechanical agitators, are made magnetic or magnetisable. During the reaction, or during the removal of the products, magnetic fields are established and broken by electrical means, so that the catalyst is kept moving, but near the exit of the apparatus a permanent field is maintained to prevent loss of the agent as dust. Examples given in the original specification include the hydrogenation of train oil, the preparation of methane from carbon monoxide, and the reduction of cinnamaldehyde to β-phenylpropaldehyde and β-phenylpropyl alcohol, lævulose to mannitol, and quinine to di- and tetra-hydroquinine. J. C. W.

**Some Problems of Atomic Stability.** J. W. NICHOLSON (*Proc. Physical Soc. London*, 1918, **30**, 65—82).—The author has investigated the dynamical stability of model atoms of pyramidal form consisting, for example, of a nucleus, a ring of electrons in the form of a circle the axis of which passes through the nucleus, and a single stationary electron on this axis. It is shown that no positively charged or neutral atom can exist in this form. Such structures are incompatible with a steady rotation of the ring electrons and cannot well form part of any molecular structure. The results appear to vitiate completely the molecular structures which have been formulated by Stark. H. M. D.

**Molecular Frequency and Molecular Number.** H. STANLEY ALLEN (*Phil. Mag.*, 1918, [vi], **35**, 338—349).—In a previous paper (compare this vol., ii, 14) it has been shown that the atomic number of an element is related to its characteristic frequency. Similar considerations have been applied to compounds, and it is shown that the formulæ $N\nu = n\nu_A$ and $N\nu = (n+\frac{1}{2})\nu_A$ represent the relations between the molecular number $N$ and the characteristic frequency $\nu$ calculated from the specific heat at low temperatures or from Lindemann's formula. In these formulæ, $n$ is an integer and $\nu_A$ the fundamental atomic frequency$=21 \times 10^{12}$(sec.$^{-1}$).

The molecular number $N$ of a compound $A_aB_bC_c$ is given by the equation $N = aN_a + bN_b + cN_c$, in which $N_a$, $N_b$, and $N_c$ are the atomic numbers of the component elements. Evidence in support of the above formulæ connecting $N$ and $\nu$ has been obtained by reference to the data for both inorganic and organic compounds. The agreement is such that the relations cannot be regarded as fortuitous.

It is suggested that the integer $n$ (the frequency number) is related to the number of valency electrons which are concerned in imparting to the solid its crystalline structure. H. M. D.

**Glauber's Period in Amsterdam.** W. P. JORISSEN (*Chem. Weekblad*, 1918, **15**, 268—271).—The register of the Western Church at Amsterdam records that "Johan Rudolph Glaubar" was interred on March 10th, 1670, proving the inaccuracy of the statement made by Goossen van Vreeswyck ("Silvere Rivier," The Hague, 1684, p. 117) that his death occurred on March 19th, 1670. A. J. W.

**Berend Coenders Van Helpen; a Groningen Alchemist of the Seventeenth Century.** F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 285—302).—An account of the life, work, and family of the alchemist Berend Coenders van Helpen, a typical landed proprietor of the seventeenth century, who was born at Groningen in June, 1601, and died at Copenhagen on January 3rd, 1678. A. J. W.

**Willem Homberg.** F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 316—337).—An account of the life and a list of the publications of Willem Homberg, who was born in Batavia on January 8th, 1652, and died in Paris on September 24th, 1715. A. J. W.

**Arrangement for Illuminating a Chemical Balance.** B. D. PORRITT (*J. Soc. Chem. Ind.*, 1918, **37**, 85T).—A "tubolite" metallic filament lamp of 16 candle-power and 8·5 inches long is fitted on the top of the balance case; the lamp is enclosed in a semi-circular aluminium reflector, which serves to direct the light through the glass top of the case on to the beam and to screen the lamp from the eyes of the person using the balance. W. P. S.

## Inorganic Chemistry.

**Production of Oxygen Free or almost Free from Chlorine.** CHEMISCHE FABRIK GRÜNAU, LANDSHOFF & MEYER, EMIL FRANKE and FRIEDRICH SCHMIEDT (D.R.-P., 299505, 1915; from *Chem. Zentr.*, 1917, ii, 508).—By the addition of a small quantity of nickel or cobalt in the form of metal, oxide, or salt, the "first period" of development of oxygen from chlorates or perchlorates is prolonged; cerium dioxide also can be used as catalyst. The last traces of chlorine can be removed from the gas by passing this through a filter of magnesium oxide, whiting, or anhydrous sodium carbonate, which may be distributed over some inert material, such as glass wool or asbestos. D. F. T.

**A Hydrogen Sulphide Generator.** L. SATTLER (*J. Ind. and Eng. Chem.*, 1918, **10**, 226).—The main generator consists of a large aspirator bottle the bottom tubulure of which is fitted with a straight stop-cock connected with one of the tubulures of a three-neck Woulfe bottle. Through the central orifice of the latter a tube passes to the bottom of the bottle and is connected by a rubber tube to an aspirator bottle placed at a higher level, which governs the pressure under which the apparatus works. The third orifice of the Woulfe bottle serves for the passage of a siphon tube with stop-cock through which the waste acid can be discharged. The upper tubulure of the main generator carries a T-piece, one branch of which is connected with a tube dipping under mercury forming a safety-valve seal against excessive pressure. The other branch of the T-piece leads the generated gas through a stop-cock to a lead pipe terminating in a perforated coil submerged in a washing bottle, through which the washed gas is delivered for use. The main generator is charged with about 23 kilos. of iron sulphide and the high-level acid reservoir with about 14 litres of hydrochloric acid diluted 1:1 by volume. On opening the stop-cocks leading to and from the main generator, the three-neck mixing bottle should be filled with acid, and about 7·5 cm. of the acid should remain in the reservoir. J. F. B.

**Synthesis of Ammonia at High Temperatures.** EDWARD BRADFORD MAXTED (T., 1918, **113**, 168—172).—From a rough calculation of the equilibrium between nitrogen, hydrogen, and ammonia, made by extending Haber's formulæ to temperatures above 1000° abs., it appears that increase of temperature leads at first to a rapid decrease in the proportion of ammonia until a minimum is reached, after which further increases cause the yield of ammonia to rise with increasing velocity. It should be possible, therefore, to realise a fair production of ammonia by heating mixtures of hydrogen and nitrogen to high temperatures and suddenly cooling the hot gases.

The subject has been examined experimentally by igniting mixtures of nitrogen, hydrogen, and oxygen in a tube (*a*) under water, so that the hot gases were cooled by the water itself, or (*b*) cooled externally by being made the tube of a Liebig's condenser. The direct cooling (*a*) proved to be far more efficient, and with a mixture of gases in the proportions $N:H:O=1:43:20$, giving a flame with temperature 2580° abs., the yield of ammonia was as much as 1·23% at atmospheric pressures.

For experimental details, see the original. J. C. W.

**Preparation of Carbon Monoxide.** BERTRAM BLOUNT (*Analyst*, 1918, **43**, 88).—Fairly pure carbon monoxide, free from carbon dioxide, may be obtained by heating a mixture of calcium oxalate and calcium oxide. The gas usually contains some sulphur dioxide if it is prepared from potassium ferrocyanide and sulphuric acid, or carbon dioxide if made from oxalic acid and sulphuric acid. W. P. S.

**Preparation of Argon in the Laboratory.** MAX BODENSTEIN and LILI WACHENHEIM (*Ber.*, 1918, **51**, 265—270).—Samples of oxygen prepared from the air usually contain argon, occasionally as much as 3%. The commercial product can therefore be used as a source of argon, the oxygen being removed by combination with hydrogen. For this purpose, the authors have designed an apparatus, which is described and figured in the text. The control of the process requires a certain amount of manipulative skill, but even on the laboratory scale it only takes about two hours to prepare a litre of argon.

The hydrogen and oxygen, supplied from cylinders with good valves, are led into a small quartz combustion chamber through gas current manometers, the water is then trapped in two condensers, and the issuing gas made to pass through a sensitive gas current manometer. If this records minimum rate of flow, it indicates that neither oxygen nor hydrogen is being supplied in excess; if not, the gases are regulated accordingly. After this manometer are placed a hot tube containing copper oxide and copper to trap any traces of uncombined gases, then another condenser for the water, and finally an iron gas-washing tube containing calcium turnings heated electrically to 600°. This serves to absorb any nitrogen that may be present.

The process is based on a method described by the Griesheim-Elektron Co., D.R.-P., 295572 of 1913. J. C. W.

**Production of Mono-, Di- and Tri-metallic Alkali Perphosphates and Perarsenates.** S. ASCHKENASI (D.R.-P., 299300, 1914; from *Chem. Zentr.*, 1917, ii, 438).—By the addition of the necessary quantity of alkali to a solution of barium peroxide in aqueous arsenic or phosphoric acid, barium arsenate or phosphate is precipitated, and the filtrate containing the per-salt is then evaporated with slight warming and under reduced pressure; an aqueous solution of a mixture of sodium peroxide with the primary or secondary alkali salts can also be submitted to evaporation. If a solution of an arsenate, phosphate, or borate in dilute hydrogen peroxide is evaporated to dryness with gentle warming and under reduced pressure, the corresponding per-salt, for example, sodium perborate, can be obtained with scarcely any loss of oxygen.

D. F. T.

**Influence of Calcium Sulphate on the Corrosive Action of Water on Iron.** P. MEDINGER (*Ber.*, 1918, **51**, 270—271).—The fact that gas and water mains suffer corrosion particularly severely in heavy clays which contain calcium sulphate is explained as follows: through the ionisation of the sulphate, the proportion of calcium ions in solution becomes so great that the dissociation of the calcium hydrogen carbonate is depressed, and, consequently, the production of H and $HCO_3$ ions from the free carbonic acid is not so much hindered. The enhanced acidity of a solution containing free carbonic acid and calcium hydrogen carbonate consequent on the addition of calcium sulphate may be demonstrated by means of litmus. J. C. W.

**Iron Trisulphide.** WERNER MECKLENBURG and V. RODT (*Zeitsch. anorg. Chem.*, 1918, **102**, 130—148).—The work of previous investigators has left undecided the question of the existence of ferric sulphide. The authors have studied the action of hydrogen sulphide on ferric hydroxide, of alkali sulphides on ferric salts, and of alkali polysulphides on ferrous salts. When hydrogen sulphide is passed for a long time (about twelve hours) through an aqueous suspension of freshly prepared ferric hydroxide at the ordinary temperature in absence of air, the colour of the hydroxide gradually becomes black, and when the reaction is finished, the composition of the precipitate corresponds with $Fe_2S_3$, aq. The precipitate contains no sulphur soluble in carbon disulphide and is completely decomposed by dilute hydrochloric acid, forming ferrous chloride, hydrogen sulphide, and sulphur. Treatment with carbon disulphide, however, changes the character of the trisulphide, rendering it partly insoluble in dilute hydrochloric acid. The hydrated trisulphide is rapidly decomposed by air, and in absence of air it undergoes spontaneous decomposition into ferrous sulphide and iron disulphide. It can be completely dried in a vacuum over phosphoric oxide. The anhydrous trisulphide is pyrophoric if suddenly brought into contact with air, but if spontaneous ignition is prevented, it is quite stable.

By addition of a solution of a ferric salt to excess of sodium sulphide solution, a precipitate is produced having the composition $Fe_2S_3,Na_2S$, and the same compound is formed by the action of excess of sodium polysulphide solution on a solution of a ferrous salt. The alkali sulphoferrites form dilute aqueous colloidal solutions having a deep green colour. E. H. R.

**Reactions in Non-aqueous Solvents. II. The Action of Chromyl Chloride on Phosphorus Haloids.** HARRY SHIPLEY FRY and JOSEPH L. DONNELLY (*J. Amer. Chem. Soc.*, 1918, **40**, 478—482).—The action of chromyl chloride on phosphorus di-iodide, tri-iodide, pentachloride, and pentabromide in anhydrous carbon tetrachloride has been examined.

With phosphorus di-iodide, a brown-coloured additive compound, $CrO_2Cl_2,PI_2$, is precipitated. It is readily decomposed by water with liberation of iodine and the formation of a solution containing phosphate, chromic, chloride, and iodide ions.

Phosphorus tri-iodide also yields an additive compound, $CrO_2Cl_2,PI_3$, which, when dry, consists of a purplish-red powder. It is decomposed by water in accordance with the equation $2CrO_2Cl_2,PI_3 + 4H_2O = 4HCl + 4HI + 2CrPO_4 + I_2$.

With phosphorus pentachloride, the additive compound $CrO_2Cl_2,PCl_5$ is produced in the form of a yellowish-red powder readily decomposed by water.

It has been previously found (A., 1916, ii, 626) that phosphorus tribromide reacts according to the equation $2CrO_2Cl_2+3PBr_3=2CrOCl,POBr_3+PBr_3Cl_2$, and the product obtained by interaction of chromyl chloride with phosphorus pentabromide appears to be a mixture of $CrOCl,POBr_3$ and the additive compound $CrO_2Cl_2,PBr_5$. The formation of these substances is presumably connected with the fact that phosphorus pentabromide is measurably dissociated into the tribromide in carbon tetrachloride solution. H. M. D.

**The Reaction between Antimony and Solutions of Sodium in Liquid Ammonia.** EDWARD B. PECK (*J. Amer. Chem. Soc.*, 1918, **40**, 335—347).—Metallic antimony dissolves when brought into contact with a solution of sodium in liquid ammonia. The atomic ratio of antimony to sodium in the saturated solution increases from about 1·2 for a solution containing 0·005 gram atom of sodium per litre to about 2·3 for a solution containing 0·4 gram atom of sodium per litre. For more concentrated solutions, the ratio diminishes slightly. The diminution may be due to the failure to reach equilibrium in the more concentrated solutions which are highly viscous, or it may possibly be accounted for by the fact that the solution was assumed to have the same volume as the ammonia which it contained.

The observed facts suggest that there are at least two compounds formed, in one of which the ratio Sb:Na is greater than two, whilst in the other this ratio is less than two.

The electrolytic behaviour of these solutions, when subjected to the action of a current between a platinum anode and an antimony cathode, has also been examined, but the quantitative data do not permit of any definite conclusion. The results show, however, that antimony is present in the solutions as anion, and that more than one atom of antimony is associated with each negative charge.

H. M. D.

**A New Metastable Form of Antimony Tri-iodide.** A. C. VOURNASOS (*Compt. rend.*, 1918, **166**, 526—528).—Antimony tri-iodide, regarded as trimorphous, may be obtained in a fourth form by cooling a hot saturated solution of the red iodide in glycerol. It is thus obtained as an amorphous, yellow powder, m. p. 172°, at which temperature it steadily passes into the red variety, forming hexagonal crystals. This metastable, amorphous form may also be obtained from the red form by warming it on a water-bath with fifteen times its weight of acetic acid and a little potassium acetate. The solution on cooling deposits the yellow, amorphous iodide. It may also be prepared from antimony trioxide and potassium iodide by heating them at 100° with an excess of anhydrous acetic acid. The last method also applies to the preparation of arsenic, antimony, and bismuth tribromides, and arsenic and bismuth tri-iodides. W. G.

# Mineralogical Chemistry.

**The Gyrohedral Character of Rock Salt.** R. GROSZ (*Centr. Min.*, 1918, 1—19).—The crystal structure deduced by W. H. and W. L. Bragg for sodium chloride and other similar salts is stated not to be satisfactory. On the one hand it is a holohedral structure, whilst there is abundant evidence that the structure of sylvine is gyrohedral hemihedral, and that other salts of the same series are certainly not holohedral; on the other hand, no account is taken of the chemical bonds between individual atoms. By symmetrically displacing the centres of gravity of selected atoms in the Bragg structure, a number of new structures can be produced having gyrohedral or tetartohedral symmetry, and it is claimed that these cannot be distinguished by *X*-ray analysis from the holohedral form. If rock salt were tetartohedral, irregularities might be expected to appear in the Laue radiogram, but such irregularities the author has failed to discover.

It has been shown by Smits and Scheffer (A., 1917, ii, 78) that it is possible to couple symmetrically the atomic valencies in a cubic structure of atoms of two kinds. The coupling leads to the formation of cubic aggregates of different sizes according to the disposition of the planes of atoms, and these aggregates may be regarded as crystal molecules. The structure derived by the association of such aggregates affords an explanation of the cubic cleavage of rock salt, since at regular intervals there occur in the series of {100} planes pairs of planes between which no chemical bonds are active. A crystal cleaved along these planes of zero affinity would contain no excess of uncombined atoms of either kind, whereas in other crystal models the "ideal" crystal always contains an excess of atoms of one kind.

The hemihedral character of the crystals of rock salt may also be accounted for by making certain assumptions regarding the axis and direction of rotation of the valence electrons about the individual atoms. E. H. R.

**Algodonite and Whitneyite.** L. H. BORGSTRÖM (*Geol. För. Förh.*, 1916, **38**, 95—100; from *Jahrb. Min.*, 1918, Ref. 11—13). —Analyses of algodonite and whitneyite from the Mohawk mine, Michigan, gave Cu 84·1 and 87·2% respectively. Melting-point determinations in capillary tubes showed a wide interval, sintering beginning at 695°, but fusion was complete only at 100° higher. These minerals are therefore decomposed before fusion takes place. The cooling curves of the fused materials show in each case a pronounced break at 688°, that is, near the freezing point (685°) of the eutectic $Cu_3As$—Cu. Polished plates of the natural minerals and of the fused products were etched with nitric acid and examined under the microscope. Algodonite was seen to consist of almost homogeneous crystalline material with very little metallic

copper, whilst whitneyite contains 3—4% of metallic copper, and thus consists of a mixture of algodonite and copper. The fused products in each case consist of a mixture of light grey $Cu_3As$ and copper. The electrical resistance in ohms for rods 1000 mm. long and 1 sq. mm. cross-section is for whitneyite 0·341 and 0·335, for algodonite 0·415, and for the fused materials 0·469 and 0·634 respectively. Although not indicated on the cooling diagrams of copper–arsenic fusions, the copper arsenide, $Cu_6As$ (algodonite), therefore exists, but is only stable below the point of fusion. On the other hand, the arsenide $Cu_9As$ (whitneyite) has no existence.
L. J. S.

**Spectral Investigation of the Composition of Goyazite.** A. DE GRAMONT (*Bull. Soc. franç. Min.*, **40**, 26; from *Chem. Zentr.*, 1917, ii, 825).—According to spectral observations, calcium, strontium, and probably aluminium are characteristic constituents of goyazite.
H. M. D.

**Meerschaum from Kraubat, Styria.** H. LEITMAIER (*Sitzungsber. K. Akad. Wiss. Wien, Math.-Nat. Kl.*, Abt. I, 1915, **124**, 163—180; from *Jahrb. Min.*, 1918, Ref. 21—22).—The meerschaum occurs as bands 1 mm. to 20 dcm. thick in massive magnesite. It is white, yellow, or green, and either earthy (being then mixed with magnesite), or compact with large-conchoidal fracture. Analysis of the latter variety gives the formula $2MgO,3SiO_2,4H_2O$. About half of this water is lost over sulphuric acid at 20°, and is reabsorbed from a moist atmosphere to the extent of 37·56% $H_2O$ after 144 hours. At 100° the loss is 9·72%, and at 450° it is 18·17%. Since $2H_2O$ is more closely held, the formula is written $2MgO,3SiO_2,2H_2O$, any extra water present depending on the vapour tension of the surrounding atmosphere. The meerschaum and magnesite have probably originated by the action of carbonated waters on serpentine. When fused, the meerschaum gives rise to an enstatite containing an excess of silica ($MgO:SiO_2=7:9$), which is probably held in solid solution.
L. J. S.

**The Identity of Shattuckite and Plancheite.** F. ZAMBONINI (*Compt. rend.*, 1918, **166**, 495—497).—The mineral shattuckite as described by Schaller (*J. Washington Acad. Sci.*, 1915, **5**, 7) and the mineral plancheite as described by Lacroix (A., 1908, ii, 508) possess the same optical and crystallographic properties, although differing slightly in their chemical analyses. As a result of the examination of a specimen of plancheite, the author has obtained analytical data in agreement with those for shattuckite and for the composition $2CuSiO_3,H_2O$, and he considers that these two minerals are identical and that the older name plancheite should be retained.
W. G.

**Gedrite from the Tatra Mountains, Hungary.** W. PAWLICA (*Bull. Acad. Sci. Cracow, Cl. Sc. Math. et Nat.*, Ser. A, 1915, 18—25; from *Jahrb. Min.*, 1918, Ref. 19—20).—Analysis I is of a gedrite-gneiss from the Gewont peak, containing quartz (41·3 mol. %), plagioclase (a basic oligoclase, $\mathrm{Ab_{72}An_{28}}$, 35·3), gedrite (13·0), biotite (5·1), ilmenite (1·3). The gedrite (anal. II, mean of three) forms black, orthorhombic prisms ½—3 cm. long and 0·1 mm. thick with distinct pleochroism, bluish-green to pale green. The high percentage of fluorine and water is not accounted for by the ordinary formula, but in Penfield's amphibole formula it figures in the molecule, $\mathrm{(F,HO)_2Mg(Al,Fe''')SiO_5}$, which is here present to the extent of 39·6%, with the metasilicate molecules, $\mathrm{MgSiO_3}$ (26·6), $\mathrm{FeSiO_3}$ (25·7), $\mathrm{CaSiO_3}$ (7·2), and $\mathrm{Na_2SiO_3}$ (0·9%).

| | $SiO_2$. | $TiO_2$. | $P_2O_5$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 69·82 | 1·24 | 0·18 | 12·70 | 2·32 | 2·78 | 0·12 | 2·96 | 2·47 |
| II. | 41·59 | 0·97 | 0·16 | 12·81 | 5·90 | 14·81 | trace | 3·55 | 15·13 |

| | $K_2O$. | $Na_2O$. | F. | $H_2O$ $<105°$. | $H_2O$ $>105°$. | Total less O for F. | Sp. gr. |
|---|---|---|---|---|---|---|---|
| I. | 0·40 | 3·27 | 0·17 | 0·23 | 1·30 | 99·89 | 3·240 |
| II. | 0·12 | 0·43 | 2·34 | 0·86 | 1·68 | 99·42 | 2·701 |

L. J. S.

**Iron Silicate Ores of the Diabase and Schalstein Zone between Sternberg (Moravia) and Bennisch (Austrian Silesia).** FRANZ KRETSCHMER (*Jahrb. Min.*, 1918, 19—42).—A detailed account is given of the characters of these ores as seen in micro-sections, an account of their chemical characters having been sent for publication in *Arch. Lagerstättenforsch., Berlin.* The dense, chloritic minerals of which these ores are composed include thuringite and moravite (A., 1906, ii, 458), and two new species, viridite and mackensite, differing from the former in containing more iron (respectively ferrous and ferric), and correspondingly less alumina. *Viridite* contains only 4·49% $\mathrm{Al_2O_3}$, and approximates to the end-member $\mathrm{4FeO,2SiO_2,3H_2O}$. It is a compact, leek-green ore, D 2·89, H 3—3½, and under the microscope is seen to consist of minute needles and scales with pearly, micaceous cleavage. *Mackensite* contains 6·14% $\mathrm{Al_2O_3}$ (in part due to the presence of admixed thuringite), and approximates to the end-member, $\mathrm{Fe_2O_3,SiO_2,2H_2O}$, of the thuringite series. It is compact, iron-black to greenish-black, D 4·89, H 3—3½, and under the microscope shows colourless or brownish-green needles surrounding shreds of thuringite and grains of calcite and magnetite. Locally, the magnetite is present in greater relative amount, but ores of this character are not abundant. L. J. S.

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## Analytical Chemistry.

**Increasing the Delicacy of Delivery of Burettes.** EWART H. MERRITT (*Analyst*, 1918, **43**, 138).—Both the inside and the outside of the jet of the burette are coated with a thin film of paraffin (m. p. about 55°); the number of drops per c.c. delivered by the burette may be thus increased from twenty to forty.

W. P. S.

**A New Process of Quantitative Analysis.** ALBERTO BETIM PAES LEME (*Compt. rend.*, 1918, **166**, 465—467).—The method is a spectrographic one, using a screen having a narrow, horizontal opening and travelling with a constant velocity in a vertical direction during the vaporisation of a known weight of the mineral containing the element to be estimated. The width of the opening and the velocity of the screen are equal. A given ray for the element is adopted once and for all, and the time during which it is visible is determined. An example is given, aluminium being the metal to be estimated.

W. G.

**Detection of Small Quantities of Chlorine in Iodine.** J. PINKHOF (*Pharm. Weekblad*, 1918, **55**, 236).—The presence of chlorine in iodine between ⅛% and 2% can be detected by neutralisation with thiosulphate and precipitation with barium nitrate of the sulphate formed.

A. J. W.

**Estimation of Chlorides in Blood.** MARCEL DUGARDIN (*Ann. Chim. anal.*, 1918, **23**, 59).—Ten c.c. of the serum are mixed with 10 c.c. of 20% trichloroacetic acid solution, the mixture is filtered, and 10 c.c. of the filtrate are diluted with 25 c.c. of water, then acidified with 5 c.c. of nitric acid, and the chloride is titrated by Volhard's method.

W. P. S.

[**Estimation of Sulphur in Ores, etc.**] F. G. HAWLEY (*Eng. and Min. J.*, 1918, **105**, 385—386).—A method is described for estimating sulphur gravimetrically in ores and furnace products by oxidation to sulphate and precipitation as barium sulphate, which avoids the difficulties usually experienced in oxidising mattes and calcines, or ores containing much copper or zinc sulphide. The oxidising mixture employed is a 20% solution of sodium chlorate to which is added a small quantity of a mixture of equal parts of bromine and glacial acetic acid, followed by an equal volume of nitric acid nearly saturated with potassium chlorate. [For details, see *Ind.*, May.]

W. F. F.

**Some Limitations of the Kjeldahl Method.** HARVEY C. BRILL and FRANCISCO AGCAOILI (*Philippine J. Sci.*, 1917, **12A**, 261—265).—The Kjeldahl method yields low results when applied to the estimation of nitrogen in pyridine, piperidine, quinoline, *iso*quinoline, hydroxyquinoline, pyrrole, and sometimes in nicotine; this is possibly due to the formation of sulphonic derivatives, which resist decomposition. In the case of pyridine, the Gunning-Arnold method gives trustworthy results if the heating is prolonged for a considerable period (four hours) after the solution has become clear. Low results are always obtained when sodium sulphate is used in place of potassium sulphate for raising the boiling point of the mixture. [See, further, *Ind.*, 225A.]

W. P. S.

**Kjeldahl's Method for the Estimation of Nitrogen.** EDUARD SALM and SIEGFRIED PRAGER (*Chem. Zeit.*, 1918, **42**, 104—105).—The addition of zinc dust is necessary in the distillation of the ammonia obtained by digesting a nitrogenous substance with sulphuric acid and mercury or with sulphuric acid, phosphoric oxide, and mercury, if potassium sulphide is not added to the sodium hydroxide. If potassium sulphide is used, zinc turnings may be used in place of zinc dust. The results obtained are too low if the zinc is omitted or replaced by aluminium. [See, further, *Ind.*, May.] W. P. S.

**Foam Inhibitor in the Van Slyke Amino-nitrogen Method.** H. H. MITCHELL and H. C. ECKSTEIN (*J. Biol. Chem.*, 1918, **33**, 373—375).—The formation of foam during the liberation of nitrogen in the Van Slyke apparatus is prevented by the addition of two or more drops of diphenyl ether, which is readily synthesised from bromobenzene and potassium phenoxide (Ullmann and Sponagel, A., 1905, i, 644). H. W. B.

**Alkalimetric Estimation of Phosphorus in Iron and Steel.** NIKOLAUS CZAKO (*Chem. Zeit.*, 1918, **42**, 53—54).—When the yellow ammonium phosphomolybdate precipitate is dissolved in a known excess of sodium hydroxide solution and the excess then titrated with standardised nitric acid, it is recommended that the latter be standardised against potassium hydrogen carbonate. The potassium hydrogen carbonate value of the acid is then multiplied by 0·013481 to obtain the phosphorus value. W. P. S.

**Separation of Phosphorus from Vanadium.** ALFRED KROPF (*Chem. Zeit.*, 1917, **41**, 877—878, 890—891).—One gram of the alloy containing phosphorus and vanadium is dissolved in aqua regia, the solution evaporated to dryness, the residue heated gently, then cooled, boiled with the addition of 20 c.c. of hydrochloric acid (D 1·12), diluted to 60 c.c., and filtered to separate silica. The filtrate is treated with 15 c.c. of ammonium citrate solution (prepared by neutralising 1 kilo. of citric acid with ammonia and diluting the solution to 5 litres), and boiled for three minutes to reduce the vanadic acid; after the addition of 30 c.c. of 40% ammonium nitrate solution and 10 c.c. of nitric acid (D 1·18), the phosphoric acid is precipitated with molybdic acid reagent. In the case of ores, the sample is fused with a mixture of sodium and potassium carbonates, or sodium carbonate and potassium nitrate, the mass dissolved in water, filtered, and the filtrate treated as described. If arsenic is present, it may be separated from the vanadium and phosphorus by treatment with hydrogen sulphide, or the phosphorus, together with some of the vanadium, may be precipitated as hydrated aluminium phosphate, and thus separated from the arsenic. W. P. S.

**Spectroscopic Detection of Boron.** A. DE GRAMONT (*Compt. rend.*, 1918, **166**, 477—480).—Boron may be readily detected if present to the extent of 1 in 10,000 by means of the ray λ 3451·2 and the doublets λ 2497·82 and 2496·87, shown in the condensed spark spectrum. W. G.

**Gasometric Estimation of combined Carbon Dioxide.** W. Mestrezat (*Ann. Chim. anal.*, 1918, **23**, 45—47).—A method for the estimation of carbon dioxide in a mixture containing a carbonate and a hypochlorite consists in treating a portion of the sample with sulphuric acid and measuring the volume of the liberated carbon dioxide after the chlorine has been absorbed by oil of turpentine. The estimation is carried out in an ordinary calcimeter, but a tube containing a plug of cotton wool impregnated with oil of turpentine is placed between the reaction flask and the gas-measuring burette. [See, further, *Ind.*, May.] W. P. S.

**Estimation of Potassium.** Bertram Blount (*Analyst*, 1918, **43**, 117—120).—For the estimation of potassium in siliceous rocks, clays, etc., the material is decomposed with hydrofluoric and sulphuric acids, iron, aluminium, manganese, and calcium are removed from the solution in the usual way, sulphuric acid is separated by treatment with barium hydroxide, and the solution is evaporated to obtain the mixed sodium and potassium chlorides. The quantity of potassium is then estimated by the platinum chloride or perchlorate method.

W. P. S.

**Calcium in Man. I. Estimation of Calcium in the Blood.** W. H. Jansen (*Zeitsch. physiol. Chem.*, 1918, **101**, 176—192).—The blood (10 c.c.) is dried and incinerated. The ash is dissolved in hydrochloric acid, nearly neutralised with ammonia, and the iron and phosphorus removed by boiling with ammonium acetate. The calcium is subsequently precipitated as oxalate from the carefully neutralised filtrate. The precipitate is collected, and, after ignition in the usual way, the residual calcium oxide is estimated by dissolving in a known volume of $N/100$-hydrochloric acid and titrating the excess with alkali or by dissolving in 15 c.c. of $N/100$-hydrochloric acid, adding 25 c.c. of water, 2 c.c. of a 10% potassium iodide solution, 4 drops of a 4% potassium iodate solution, and 2 drops of a 1% starch solution in 20% potassium chloride solution, and then titrating with $N/100$-thiosulphate solution until the blue colour just disappears. H. W. B.

**Estimation of Hardness of Water by the Method of Wartha-Pfeiffer.** Wagner (*Zeitsch. öffentl. Chem.*, 1917, **23**, 375—379. Compare A., 1914, ii, 490).—This method yields more trustworthy results, particularly in the case of waters containing relatively large quantities of magnesium salts, if the amounts of sodium carbonate and sodium hydroxide in the reagent are increased to 14·5 grams and 8·01 grams per litre, respectively.

W. P. S.

**Estimation of Sulphur and Copper Oxide.** C. G. Maier (*Eng. and Min. J.*, 1918, **105**, 372—373).—For estimating the proportions of copper sulphide and "oxide" or soluble copper in a sample of copper ore, especially for use in flotation processes, the ore is heated with 4% sulphuric acid at 80—90°, the mixture cooled, and clean mercury added and mixed thoroughly with the residue so that it amalgamates with the metallic copper present or reduced from cuprous oxide. The solution is filtered, and the copper determined separately in the filtrate and residue, preferably by the iodide method. The copper in the residue represents the sulphide and that in the solution the "oxide" or soluble copper. [See, further, *Ind.*, May.] W. F. F.

**Copper Dicyanodiamide and its Use in Analysis.** H. Grossmann and J. Mannheim (*Chem. Zeit.*, 1918, **42**, 17—19).—Copper may be precipitated by treating a solution of one of its salts with concentrated dicyanodiamide sulphate solution, rendering the mixture slightly ammoniacal, heating it to boiling, and then adding sodium hydroxide solution until the blue colour changes to reddish-violet. After cooling, the red precipitate is collected, washed with cold water, and dried at 120°; it contains 23·92% of copper. As the precipitate is slightly soluble in water, all the solution used should be concentrated. Nickel may be precipitated in a similar way (compare A., 1907, ii, 819), and the method may be used for the separation of copper and nickel from zinc, aluminium, chromium, arsenic, lead, and antimony. In exceptional cases, where the introduction of alkali into the solution is not desired, dimethylamine may be used in place of sodium hydroxide to precipitate the copper and nickel compounds. W. P. S.

**Analysis of Aluminium Alloys.** Bernard Collitt and William Regan (*J. Soc. Chem. Ind.*, 1918, **37**, 91—94T).—Methods are given for the estimation of copper, iron, nickel, manganese, zinc, magnesium, and silicon in aluminium alloys such as are used in the construction of aircraft and other engines of warfare. In cases where the alloy contains only copper (10 to 15%) and manganese (1%) in addition to aluminium, the copper may be estimated volumetrically by the iodide method; in other alloys it is estimated gravimetrically by precipitation as sulphide by thiosulphate, the sulphide being subsequently ignited and weighed as oxide. The original should be consulted for the details of the methods recommended for the estimation of the other constituents. W. P. S.

**Volumetric Estimation of Manganese by means of Sodium Arsenite.** Fred Ibbotson (*Chem. News*, 1918, **117**, 157—158).—When permanganate solution containing nitric acid is titrated with sodium arsenite solution, the latter has a reducing value about 33% in excess of the value it has when used against potassium permanganate solution alone. This appears to be due to the formation of manganic compounds in the presence of nitric acid. [See, further, *Ind.*, May.] W. P. S.

tains ethyl alcohol) with permanganate, and the colorimetric estimation of the formaldehyde thus obtained by oxidation under standard conditions by magenta-sulphurous acid solutions.

A new method is also given for determining the presence of methyl alcohol when it is only present in small quantities. The essential process consists in the fractional separation of the mixed methyl and ethyl alcohols by potassium carbonate. The alcohol separated first by incomplete saturation with the carbonate contains scarcely any methyl alcohol. After separation of fractions containing only minute amounts of methyl alcohol, the residue is distilled. The distillate is fractionated, and the first fractions are redistilled. These fractions are again redistilled, the earlier fractions only being retained. A fraction is finally obtained which is rich in methyl alcohol, and this, after drying over calcium oxide, is converted into iodides, from which a fraction rich in methyl iodide can be separated.

It is shown that the methyl alcohol in certain spirits is derived chiefly from the pectin substances, from which 10—11% of methyl alcohol can be separated by treating with dilute sodium hydroxide.

The lignins of wood also yield methyl alcohol, but this is not eliminated so readily as that of pectins. It can be obtained in various fractions by treating the wood first with sodium hydroxide to eliminate the pectin alcohol, and then with graded strengths of sulphuric acid. Each filtrate obtained in this way is then treated with 70% sulphuric acid, and the methyl alcohol in the distillate is estimated, as well as the methyl alcohol in the distillate, before treatment with the 70% acid.

The methyl alcohol of the pectins and lignins was determined in a large number of different kinds of woods, etc.

An investigation was also made of the effect of ingestion of substances containing pectins. The ingestion of pectin-containing substances caused a small increase in the excretion of methyl alcohol in the urine, which was much more marked when ethyl alcohol was ingested at the same time. It was suggested that certain symptoms found in the drinkers of spirits may be due to the methyl alcohol contained therein. [See also *Ind.*, May.] S. B. S.

**Estimation of Glycerol by Wagenaar's Method.** J. H. M. Beckers and I. M. Kolthoff (*Pharm. Weekblad*, 1918, **55**, 272—281).—Wagenaar's method of estimating glycerol (A., 1911, ii, 663) gives results dependent on the composition and temperature of the liquid. Methyl alcohol is without influence on the reaction, but the presence of ethyl alcohol, haloids, nitrates, and to a less degree sulphates, is deleterious. With fats, it is best to saponify with methyl-alcoholic potash and remove the fatty acids with the minimum quantity of sulphuric acid. A. J. W.

**Estimation of the Amount of Water in Glycerol.** I. M. Kolthoff (*Pharm. Weekblad*, 1918, **55**, 304—307).—An account of a method of estimating the percentage of water in glycerol by observing the temperature range of complete miscibility of mixtures of the sample and aniline. A table showing the corresponding percentages of water is given. A. J. W.

**Methylene-blue a Sensitive Reagent for the Detection of Picric Acid in Urine.** ROZIER (*Bull. Sci. Pharmacol.*, 1917; from *Ann. Chim. anal.*, 1918, **23**, 63).—The urine is treated with normal lead acetate and filtered; 4 c.c. of the filtrate are placed in a test-tube, one drop of 0·5% methylene-blue solution is added, and the mixture is shaken with 1 c.c. of chloroform. After separation, the chloroform layer has a green colour if picric acid or picramic acid is present in the urine; in their absence, the chloroform is coloured blue. The test will detect the presence of 2 mg. of picric acid per litre of urine. W. P. S.

**Colorimetric Estimation of Picric Acid and its Derivatives in Body Fluids.** X. LAPORTE (*Bull. Soc. Pharm. Bordeaux*, 1917, No. 3; from *Ann. Chim. anal.*, 1918, **23**, 64).—A definite volume of the fluid (which should be diluted or concentrated so that it contains about 0·01 gram of picric acid per litre) is neutralised and treated with 0·5 c.c. of ferrous sulphate–tartaric acid reagent (compare A., 1917, ii, 158) and 1·5 c.c. of ammonia; these quantities of reagents are required for each 10 c.c. of the sample. The coloration obtained is compared with that produced by a known amount of picric acid under the same conditions. W. P. S.

**Estimation of Cholesterol.** I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1918, **101**, 89—98).—The author finds that the method described by Windaus (A., 1909, i, 172) for recovering the cholesterol or similar component from the digitonin–cholesterol complex is unsatisfactory. By the following procedure, a quantitative separation is effected. About 0·5 gram of the anhydrous complex is weighed out and boiled with 5 c.c. of acetic anhydride for twenty to thirty minutes under a reflux condenser. The hot liquid is poured into about 80 c.c. of water. After the product of the reaction has solidified, it is collected, washed, and dried in a vacuum. It is now removed as completely as possible from the filter paper, transferred to a small flask, dissolved in 10 c.c. of 90% alcohol, and mixed with 10 c.c. of 1% aqueous sodium hydroxide. The resulting emulsion is boiled for two and a-half to three minutes, cooled, diluted with water, acidified, and extracted with ether. The cholesteryl acetate dissolves in the ether, whilst the digitonin remains in the dilute alcohol. After evaporation of the ether, the cholesteryl acetate is hydrolysed with alcoholic potassium hydroxide, and the free cholesterol or similar compound extracted by ether, weighed, and subsequently identified in the usual way. H. W. B.

**Detection of Acetone in Urine.** HANS TRUNKEL (*Pharm. Zeit.*, 1918, **63**, 104—105).—Legal's nitroprusside test is trustworthy and gives the best results when applied as a ring test. Two c.c. of the urine are mixed with ten drops of 20% sodium nitroprusside solution and 1 c.c. of acetic acid, and 2 c.c. of ammonia are poured on the surface of the mixture; if acetone is present, a violet-red zone appears at the junction of the two liquids. Reichardt's test (A., 1916, ii, 119), in which the acetic acid of the Legal test is replaced by ammonium chloride, is less trustworthy, since a feeble coloration is obtained in the absence of acetone. It is not necessary for the nitroprusside solution employed to be freshly prepared; the solution, if made with the pure salt, keeps almost indefinitely. W. P. S.

**Estimation of Pyridine Bases in Ammonia and its Salts.** T. F. HARVEY and C. F. SPARKS (*J. Soc. Chem. Ind.*, 1918, **37**, 41—43T).—The pyridine is precipitated as periodide from a sulphuric acid solution of the sample (ammonia, ammonium carbonate, or other salt) in the presence of sodium chloride, the periodide is converted into sulphate, and the latter titrated with alkali solution. When sufficient sodium chloride is added, 1 mg. of pyridine in 200 c.c. of *N*/2-sulphuric acid is precipitated completely as periodide. The method in detail is as follows: Fifty c.c. of the sample of ammonia (D about 0·885) is treated, in a separating funnel provided with a plug of cotton wool above the tap, with 100 c.c. of 10*N*-sulphuric acid, the mixture being cooled during the addition of the acid. Fifty grams of sodium chloride are then dissolved in the mixture, and 10 c.c. of iodine solution (iodine, 13 grams, and potassium iodide, 13 grams, per 100 c.c.) are added. The mixture is shaken, and, after fifteen minutes, the liquid portion is forced through the cotton wool filter; the precipitate is washed with 20 c.c. of a mixture of 10*N*-sulphuric acid, 10 c.c., water, 190 c.c., and iodine solution (see above), 10 c.c., then decomposed by a slight excess of saturated thiosulphate solution, diluted to about 20 c.c., and neutralised with *N*/1-sodium hydroxide solution, using methyl-orange as indicator. Phenolphthalein is then added, and the pyridine sulphate titrated with *N*/10-sodium hydroxide solution; 1 c.c. of the latter is equivalent to 0·0079 gram of pyridine. The solution employed for washing the periodide precipitate should be made about eighteen hours before using and be filtered if necessary. W. P. S.

**Colour Reactions in the Chemico-legal Examination of Bloodstains.** LUCIANO P. J. PALET and AMANCIO FERNANDEZ (*Anal. Soc. Quim. Argentina*, 1917, **5**, 177—184).—A review of the various colour tests proposed for the identification of bloodstains. A. J. W.

# General and Physical Chemistry.

**The Optics of Disperse Systems. I.** I. LIFSCHITZ (*Kolloid Zeitsch.*, 1918, **22**, 53—57).—A general discussion of the optical properties of disperse systems, including the absorptive power, the refractivity, and the rotatory power of optically active colloids.

H. M. D.

**The Relation between the Degree of Supersaturation, the Refractive Index and the Temperature of Sugar Solutions.** E. V. MILLER and F. P. WORLEY (*J. Soc. Chem. Ind.*, 1918, **37**, 98—103T).—Measurements have been made of the refractive index of supersaturated solutions of sucrose with the object of determining the influence of temperature and concentration on the refractive index between 30° and 75° and between 72% and 81% of sucrose, which range of concentration is of technical importance. The results obtained show that the refractive index, in its dependence on the temperature $t$ and the percentage concentration $p$, can be satisfactorily represented by the equation $r = 1{\cdot}28534 - 0{\cdot}0001241t + (0{\cdot}00263 - 0{\cdot}000001267t)p$. This equation may be written in an alternative form, in which $r$ is represented as a function of the temperature and the degree of supersaturation $s$, the relation between $p$ and $s$ being given by $p = 100(S+s)/100+S+s$, in which $S$ represents the number of parts of sucrose per 100 of water in the saturated solution. A table is given showing the values of the refractive indices of solutions for $s=0$ to $s=110$, and for temperatures ranging from 43·3° to 76·6°. H. M. D.

**The Arc Spectrum of Europium and a New Element, Eurosamarium, between Europium and Samarium.** JOSEF MARIA EDER (*Sitzungsber. K.K. Akad. Wiss. Wien*, 1917, IIA, **126**, 473—531; from *Chem. Zentr.*, 1918, i, 70—71).—Europium imparts a fine red colour to the electric arc, and its characteristic groups of lines are very bright and easily distinguished. The author has examined the photograph of the spectrum of one of Urbain's preparations, which proved to be remarkably pure, and has also tested two samples supplied by Auer, the one being a europium fraction related to gadolinium and the other a specimen akin to samarium. In these, he has measured 1171 europium lines between 7370 and 2373. The lines which were obtained with the material quite free from samarium included some which are ascribed to a new element, *eurosamarium*, and these are tabulated in the original. J. C. W.

**Atomic Weights of the Elements in Nebulæ.** J. W. NICHOLSON (*Month. Not. Roy. Astr. Soc.*, 1918, **78**, 349—362).—A theoretical paper in which equations are derived for the periods of vibration of atoms with a single ring of electrons. These equations, in combination with the wave-lengths of the principal lines in the spectrum of nebulium, give for $m/M$ the value 0·000415, in which $m$ is the mass of an electron and $M$ the mass of the atom. Assuming that for hydrogen $m/H = 0{\cdot}000545$, the atomic weight of nebulium is found to be 1·31, with a possible error of one unit in the second decimal place. H. M. D.

**The Shifting of Radioactive Equilibria under the Influence of Fluorescein.** H. Zwaardemaker (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 768—772. Compare A., 1917, i, 241).—The antagonism between potassium and uranium in their influence on the pulsation of the frog's heart is found to be appreciably affected by the addition of fluorescein in the sense that a larger quantity of potassium is required to antagonise a given quantity of uranium if fluorescein is added to the solution. The displacement produced by fluorescein is in the same direction as that which, according to observations on summer and winter frogs, is produced by a rise of temperature. H. M. D.

**Radioactivity of Waters of the Mountainous Region of Northern Luzon (Philippines).** George W. Heise (*Philippine J. Sci.*, 1917, **12**, [A], 293—307).—In continuation of previous work (Wright and Heise, A., 1917, ii, 560), the author has examined the waters of a number of springs and wells in northern Luzon. The region shows evidence of recent vulcanism. The data are not yet numerous enough to warrant general conclusions, but they do not confirm the usual observation that radioactivity is most common among waters from volcanic regions, or at least among thermal springs. Of the numerous salt springs and hot springs examined, none showed high radioactivity. The most active waters were rich in calcium and magnesium, indicating an origin in calcareous material. High activity was found only in waters from a small district (Ifugao), and was probably due to the presence of local deposits of radioactive material. J. H. L.

**Constancy in the Radioactivity of certain Philippine Waters.** George W. Heise (*Philippine J. Sci.*, 1917, **12**, [A], 309—311).—Measurements of the radioactivity of the water of a Philippine spring at different periods of the year showed no appreciable changes, in spite of great variations in the rate of flow of the spring. The composition of the water is substantially the same as in 1890. J. H. L.

**Extrapolation of Conductivity Data to Zero Concentration.** James Kendall (*J. Amer. Chem. Soc.*, 1918, **40**, 622—623).—Polemical, in which the author claims priority over Washburn (this vol., ii, 55) in the method employed by the latter for the calculation of the zero concentration values of conductivity data. [See T., 1912, **101**, 1279, 1291.] J. F. S.

**Electrolytic Dissociation in Solvents with Low Dielectric Constants.** V. A. Plotnikov (*Reprint*).—From theoretical considerations and the results of conductivity measurements on various solutions, the following conclusions are drawn. Solvents with low dielectric constants are capable of forming solutions showing high electrical conductivity. The conductivity of a solution depends to as great an extent on the solute as on the solvent; these two must be in peculiar electrochemical correspondence in order that they may yield a conducting solution. The phenomenon of electrical conductivity in a solution cannot be explained by any definite property of the solvent conditioning its dissociating capacity; electrochemical investigation of a solution has to deal with a conducting "couple." Electrochemical correspondence is explained as due to the resonance of the movement of the solvent molecules with the ionic vibrations of the electrolyte. T. H. P.

**Electrochemical Potential and the Periodic Law.** J. C. Thomlinson (*Chem. News*, 1918, **117**, 176).—The relation between electrochemical potential and the position of the elements in the periodic system is demonstrated by means of a curve. In this curve, starting with the most electropositive element, cæsium, the elements follow the order cæsium to lithium (as in group I), barium to magnesium (as in group II), aluminium, chromium, manganese, zinc, cadmium, iron, cobalt, nickel, hydrogen. The non-metals then continue the curve, and these, after silicon, carbon, and boron, all occupy positions in the upper right-hand corner of the periodic table. J. F. S.

**The Passivity of Chromium.** A. H. W. Aten (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 812—823).—The values recorded in the literature for the potential of the chromium electrode are very divergent, and this is supposed to be connected with the tendency of the metal to assume the passive condition. Electrodes were prepared from chromium obtained by Goldschmidt's method, by the electrolysis of solutions containing a mixture of chromic sulphate and chromic acid, and by the electrolysis of solutions of chromic chloride. These were brought into contact with a 0·3 molar solution of chromous sulphate and combined with a normal calomel electrode.

The results obtained indicate that the potential of chromium in contact with chromous sulphate solution is about −0·75 volt, or −0·47 volt when referred to the hydrogen electrode. This active potential value is only attained when hydrogen is present in the metal in sufficient quantity. The hydrogen appears to act as a catalyst in promoting the establishment of the electrode equilibrium. H. M. D.

**Potential Measurements on the Copper-Nickel Series of Alloys and some observations on Brasses.** Newell T. Gordon and Donald P. Smith (*J. Physical Chem.*, 1918, **22**, 194—215).—A study of the factors affecting the potential difference between a binary (solid) alloy and an electrolyte containing the corresponding ions (see A., 1916, ii, 214). With copper–zinc alloys, no treatment employed was sufficient to ensure reproducibility or constancy in the "steady" potential finally attained, but copper–nickel alloys are shown to be very regular in electrochemical conduct, and the potential values are reproducible and constant for many hours.

Six ingots of copper–nickel alloys, containing 6·8, 10·9, 65·5, 74·3, 83·4, and 94·7% of Cu were carefully prepared, and a small test-piece $2 \times 2 \times 2\frac{1}{2}$ mm. cut from each, the end surface of each bar forming a portion of a horizontal plane passing through the middle of the ingot, and this was the part exposed afterwards to the electrolyte. Each piece was annealed in an atmosphere of nitrogen, the first two at 218° and the others at 600°. The electrolytes employed were all $N/1$-solutions of copper and nickel sulphates combined, and some contained in addition $N/1$-sodium sulphate. All potentials were measured at 25° against a normal calomel electrode by means of a potentiometer and a galvanometer. For some time after immersion the potential changes rapidly, but after some hours a steady value is reached, which afterwards remains constant within 3 millivolts during the period of observation. It is found that carefully annealed specimens give the most constant results, and although there are no regular differences between the steady potentials of surfaces annealed and treated with emery, yet the latter exhibit greater accidental variations. Polished surfaces have a greater tendency to give ions to the solution. With alloys from a given ingot, and also with ingots of a similar composition, it was found that the steady potential is definitely determined by the composition of the electrolyte. The potential differences exhibited are expressible by a relation which is linear both with respect to alloy composition and to the logarithm of electrolyte composition.

It is shown that copper sulphate concentration may be employed without any sacrifice of accuracy in the representation of the empirical results in place of the cupric ion concentration required by Nernst's thermodynamic theory, provided the constants of the equation are altered. B. N.

**The Lead Electrode. II.** FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 611—619).—Since the publication of the previous paper (A., 1916, ii, 287), the question of the possible allotropy of lead has arisen. The present work was undertaken to furnish an answer to this question. The *E.M.F.* of cells of the type $Pb|0{\cdot}1M KCl$ sat. with $PbCl_2 || 0{\cdot}1M KCl, Hg_2Cl_2 | Hg$ has been measured at 25°, using lead electrodes from various sources and treated in different ways. It is shown that the value of the *E.M.F.* obtained with different specimens of lead cast into sticks, with electrolytically deposited lead, and with lead amalgams, was the same in all cases. The normal electrode potential of lead was calculated from the results to be 0·4121 volt referred to the

$N$-calomel electrode and 0·1293 volt against the $N$-hydrogen electrode. The values of the *E.M.F.* of cells containing electrodes which had been immersed for varying periods of time in Heller's solution (400 grams lead nitrate, 1000 c.c. water, and 100 c.c. nitric acid [D 1·16]) were found to be about 8 millivolts higher than the values obtained with cells containing electrodes which had not been subjected to this treatment. The temperature coefficient of the cell was found to be 0·00022. The heat of the reaction $Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$ was calculated, and found to be 21,840 cal., and the heat of formation 84,440 cal. The heat of reaction $U_0$ and the maximum work $A_{234°}$ were calculated by means of the Nernst-Lindemann equation, and the value of the *E.M.F.* at 234° *A* computed. The values $U_0 = 24.035$ cal., $A_{234°} = 24,041$ cal., were obtained, and the value of the *E.M.F.* was in close agreement with the experimental value. J. F. S.

**The Quantum Theory of Paramagnetism.** FRITZ REICHE (*Ann. Physik*, 1917, [iv], **54**, 401—436).—A mathematical paper in which the quantum hypothesis is applied in the development of a theory of paramagnetism. The formula derived for the relation between the magnetic susceptibility and the temperature is tested by reference to the available data for ferrous sulphate and manganous sulphate, and found to be quite satisfactory. H. M. D.

**Investigations on the Thermal Conductivity of Gases. I. and II.** SOPHUS WEBER (*Ann. Physik*, 1917, [iv], **54**, 325—356, 437—462).—The sources of error involved in the determination of the thermal conductivity of gases by Schleiermacher's method are subjected to a critical analysis, and a modified form of apparatus is described in which the errors due to convection are greatly reduced. With this improved form of apparatus, measurements have been made of the thermal conductivity of a number of gases.

The following values are recorded: hydrogen, $4·165 \times 10^{-4}$; neon, $1·089 \times 10^{-4}$; helium, $3·438 \times 10^{-4}$; argon, $3·850 \times 10^{-5}$; nitrogen, $5·660 \times 10^{-5}$; oxygen, $5·768 \times 10^{-5}$; methane, $7·200 \times 10^{-5}$; carbon dioxide, $3·393 \times 10^{-5}$; nitrous oxide, $3·530 \times 10^{-5}$. The results are discussed in reference to certain aspects of the theory of the conductivity of gases. H. M. D.

**The Course of the Values of *a* and *b* for Hydrogen at Different Temperatures and Volumes.** J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 750—767).—A theoretical paper in which the author discusses the influence of temperature and volume on the constants *a* and *b* of the van der Waals's equation. It has been suggested by van der Waals that *a* varies with the volume if the temperature is lower than the critical temperature, but the author's arguments lead to the conclusion that *a* depends only on the temperature, whether this is above or below the critical temperature. On the other hand, *b* appears to be a function of both temperature and volume.

H. M. D.

**The Saturated Vapour Pressures of Triatomic Liquids.** E. ARIÈS (*Compt. rend.*, 1918, **166**, 668—672. Compare this vol., ii, 61).—Using the known physical constants for carbon dioxide, the author deduces the formula $\Pi = \tau^{14/5} Z/x$, where $x = [1 + (1 - \tau)(0{\cdot}88 - \tau)/0{\cdot}40(\tau^2 + 1)]\tau^{9/5}$ for the saturated vapour pressures of triatomic liquids. The observed results are in fairly close agreement with those calculated by this formula in the cases of sulphur dioxide and nitrous oxide, but this is not true for hydrogen sulphide and water. W. G.

**The Adsorption of Sodium Gold Chloride by Charcoal. The Estimation of Gold in Sea-water.** HELLMUTH KOCH (*Kolloid Zeitsch.*, 1918, **22**, 1—22).—The adsorption of gold from very dilute solutions of gold chloride in 3% sodium chloride by various forms of carbon has been examined with a view to the application of the adsorption process in the estimation of gold in sea-water. Measurements of the rate of the adsorption show that this takes place fairly rapidly, but the attainment of a condition of equilibrium is prevented by the fact that the adsorbed gold salt is slowly reduced, and in consequence of this there is a continuous fall in the concentration of the gold in the aqueous solution. The concentration time curve consists accordingly of two branches of very different slopes, the intersection of which affords a sufficiently accurate measure of the adsorption effect.

The results obtained for solutions of varying concentration are satisfactorily represented by means of the ordinary adsorption equation. Finely divided wood charcoal was found to be the most satisfactory adsorbent, and this material was used in experiments on sea-water, three samples of which gave results indicating the presence of 2·5 to 4 mg. of gold per cubic metre. These values for the quantity of gold in sea-water are in agreement with the results obtained by some earlier observers, although much larger values have been recorded. The literature of the subject is discussed in detail. [Compare *J. Soc. Chem. Ind.*, June.] H. M. D.

**Influence of Neutral Salts on the Dissociation Constants of Indicators.** I. M. KOLTHOFF (*Chem. Weekblad*, 1918, **15**, 394—400).—The dissociation constants of phenol, aniline, and colorimetric indicators are increased by addition of neutral salts. This fact explains the development of the alkaline tint on addition of a neutral salt to an acid indicator, and the corresponding development of the acid tint of an alkaline indicator. The effect is very marked in the case of azolitmin. A. J. W.

**[Diffusion of Gases through Indiarubber.]** SIR JAMES DEWAR (*Proc. Roy. Inst.*, 1918, **21**, 813—826).—An appendix to a lecture on "Problems of Hydrogen and the Rare Gases" (compare *ibid.*, 543). An account is given of apparatus which has been used by the author in the investigation of the diffusion of gases through thin rubber membranes at varying pressures and temperatures.

With a membrane about 0·01 mm. thick, the rates observed for different gases, at atmospheric pressure and 15°, in c.c. per day per cm.$^2$ were: air, 2·0; nitrogen, 1·38; carbon monoxide, 1·88; helium, 3·5; argon, 2·56; oxygen, 4·0; hydrogen, 11·2; carbon dioxide, 28·0. The order in which the gases are arranged according to their diffusibility does not appear to be directly related to any chemical or physical property of the gases concerned.

The rate of diffusion increases rapidly with rise of temperature, and when the logarithm of the rate is plotted against the temperature, straight line graphs are obtained. These lines all show a distinct break at 0°, which suggests that water is in some way involved. In the case of carbon dioxide, a much more pronounced break is found at $-37°$.

The composition of the gaseous mixture resulting from the diffusion of air through rubber has been examined by ordinary chemical analysis and also by the spectroscopic investigation of the residue obtained after subjecting the mixture to the action of charcoal cooled in liquid air. By this means, it has been found that the hydrogen and helium in air diffuse at nearly the same rate, whilst the rates of diffusion of helium and neon are as 9 to 1.

Observations were also made on the diffusion of gases through rubber membranes immersed in different liquids, such as water, salt solutions, ethyl alcohol, and glycerol. H. M. D.

**Diffusion in Anisotropic Liquids.** THE. SVEDBERG (*Kolloid Zeitsch.*, 1918, **22**, 68—71).—In view of the necessity of maintaining a constant temperature in the diffusion experiments, the author has made use of an equimolecular mixture of *p*-azoxyanisole and *p*-azoxyphenetole. This mixture, which melts at 95° and becomes isotropic at 150°, is convenient for the observations in that the diffusion measurements may be made at 100°. The rate of diffusion of *m*-nitrophenol in the anisotropic liquid was measured (*a*) in the absence of an external magnetic field, (*b*) in a longitudinal magnetic field, and (*c*) in a transverse magnetic field. The results obtained show that the rate of diffusion is increased by the application of the longitudinal field and diminished when the direction of the field is transverse to that in which diffusion takes place. H. M. D.

**Kinetic Theory of Osmotic Pressure and of Raoult's Law. II.** G. JÄGER (*Ann. Physik*, 1917, [iv], **54**, 463—480. Compare A., 1913, ii, 762).—A theoretical paper devoted to the consideration of the kinetic interpretation of osmotic pressure and of Raoult's vapour pressure law. H. M. D.

**Manifestation of Osmotic Pressure with Membranes of Chemically Inert Materials.** S. L. BIGELOW and C. S. ROBINSON (*J. Physical Chem.*, 1918, **22**, 153—183).—A method and apparatus have been devised for the study of osmotic phenomena with membranes of powdered materials, such as silica, amorphous carbon, graphite, metallic copper, gold, and silver. The membranes were prepared by alternately pressing the purified material under a high pressure and clogging the pores by sucking a fine material in suspension through the membranes. Thus, in the case of pure silica, a pressure of 350 kilos. per cm. was used, and the largest pores in two membranes were reduced to 1·4823 and 0·3488 microns respectively. Amorphous carbon was prepared by ignition of a pure sucrose, compressed, and clogged as above, but the pore diameters in this, and in flaky graphite washed with acid and similarly treated, had to be considerably reduced to produce osmosis. Reduced copper and silver powders had to be pressed for several days at 350—450 kilos. per cm. to reduce the diameters, and the results show generally that the magnitude of osmotic effects increases with a decrease in the diameters of the pores of the membrane. It appears to be fairly obvious that the various examples of osmosis are not due to one but to a variety of causes, and according to the various theories osmosis may take place (1) through capillary spaces in the membrane, (2) by solution of the solvent in the membrane, (3) by the formation of a labile chemical compound between the membrane and the solvent. The present work has demonstrated that osmotic pressure can be produced through the agency of capillary forces alone, without the aid of solution processes or chemical reactions.

B. N.

**Theory of Solutions. Solubility Studies in Ternary Mixtures of Liquids.** John Holmes (T., 1918, **113**, 263—275, Compare T., 1913, **103**, 2147).—In the further investigation of the theory that the miscibility of liquids is determined by the possibility of the close-packing of the different kinds of molecules, and is therefore dependent on the relative molecular radii, the author has examined a number of three-component systems.

The theory indicates that these liquids should be miscible in all proportions if the molecular radii are equal. If the molecules are of different sizes, the dimensions of the interspaces will decrease as the ratios between the several radii increase until a point is reached at which close packing is a maximum. In the case of an equimolecular mixture this occurs when the radii are as 1·682 : 1·466 : 1. If the respective ratios are greater than these limiting values which correspond with the border line between complete and partial miscibility, separate layers are formed.

So long as the radial ratio of the two smaller molecules is not greater than 1·618 and the corresponding ratio for the extreme molecules exceeds 1·682, but is less than $(1·618)^2$, the mixture should separate into two layers only. If the ratios are greater than these values, three separate layers are to be expected.

In the expectation that the higher paraffin hydrocarbons would afford liquids for which the molecular radii compared with water are greater than $(1·618)^2$, the author has examined the miscibility of various binary mixtures of petroleum and water with a third substance. Three-layer systems were obtained with aniline, phenol, nicotine, and nitrobenzene, and the behaviour of these mixtures is described.

Three liquid layers were also found in the case of mixtures of petroleum, glycerol, and nitrobenzene. H. M. D.

**Condition of Substances in Solution in Absolute Sulphuric Acid. VIII.** G. Oddo [with A. Casalino]. (*Gazzetta*, 1918, **48**, i, 17—44).—The author uses the results of his previous measurements, some of which have now been repeated and confirmed, to refute the criticisms of Hantzsch (*ibid.*, 1911, **41**, i, 645). T. H. P.

**Flocculation.** Spencer Umfreville Pickering (*Proc. Roy. Soc.*, 1918, [*A*], **94**, 315—325).—Experiments have been made to determine the effect of freezing on the sedimentation of certain voluminous precipitates, such as basic copper sulphate, cupric hydroxide, ferric hydroxide, and aluminium hydroxide, and also on clay and kaolin. In all cases, sedimentation takes place more rapidly after freezing, and the volume of the sediment from the liquids which have been frozen is considerably smaller than that from liquids which have not been subjected to this treatment. The shrinkage observed varies from 40 to 90%, and is probably due to dehydration.

The flocculation of suspensions of kaolin on the addition of various substances has been examined, with results which show that the process is accompanied by a considerable increase in the volume of the particles. The increase in the volume of the sediment when acids or salts are used as the flocculating agents is closely related to the quantity of kaolin remaining in suspension, the latter becoming nil when the former reaches a maximum. When the added substance produces no flocculation, there is no increase in the volume of the sediment. In explanation of these relations, it is suggested that the kaolin combines with the flocculant. H. M. D.

**Jellies Formed by Dyes.** R. Haller (*Kolloid Zeitsch.*, 1918, **22**, 49—57).—It has been observed that hot concentrated solutions of substantive dyes produce jellies when the solutions are allowed to cool. Experiments made with benzopurpurin 4 B and chrysophenin B show that the formation of these jellies is dependent on the presence of small quantities of electrolytes in the dyes. If a 1% solution of either of the dyes is subjected to dialysis, the electrolytes are removed and the contents of the dialyser separate into two parts, one of which is liquid and the other of gelatinous consistency. The latter does not dissolve even when heated to 100°, and it seems probable that the colloidal dye has been rendered insoluble by the removal of the electrolytes. If the dialysed substance is dried and powdered, the product is markedly different from the original dye in its small solubility in water. The purified substance dissolves quite readily, however, if sodium chloride is added to the water.

The structure of the benzopurpurin 4 B jellies has been examined and found to be very similar to that of the soap jellies described by Zsigmondy and Bachmann (A., 1912, ii, 1149). [See, further, *J. Soc. Chem. Ind.*, June.] H. M. D.

**The Quaternary System, $AgNO_3$-$NH_4\cdot NO_3$-$Ba(NO_3)_2$-Water at 30°.** (Miss) W. C. de Baat (*Chem. Weekblad*, 1918, **15**, 463—468).—An application of Schreinemakers's graphic method to aqueous solutions of the nitrates of silver, ammonium, and barium at 30°. A. J. W.

**A Method of Obtaining General Reaction-Velocity Curves for Complete Homogeneous Gas Reactions at Constant Pressure.** George W. Todd (*Phil. Mag.*, 1918, [vi], **35**, 435—444. Compare this vol., ii, 102).—The method previously described for the derivation of curves representing the progress of homogeneous reactions at constant volume has been extended to the case of binary gas reactions taking place at constant pressure.

For a bimolecular reaction of the type $A+B\longrightarrow$, in which $a$ gram mols. of $A$ react with $b$ gram mols. of $B$, $v$ is the total volume of reactants and resultants, and $x$ the number of gram mols. transformed in time $t$, the equation for the velocity of the reaction when $B$ is in excess may be written in the form $dX/dt=k\,.\,a/v_0\,.\,(1-X)(p-X)$, where $X=x/a$, $p=b/a$, and $v_0$ is the original value of $v$. Since the right-hand side of this equation does not involve the constant, which, in a particular case, is determined by the ratio between the numbers of mols. of reactants and resultants, it follows that the general curves previously given will be applicable to the case of bimolecular reactions at constant pressure as well as at constant volume.

Termolecular reactions of the type $2A+B\longrightarrow$ with $A$ and $B$ in excess are also considered, and general equations devised for these. The curves which are plotted from these equations show the change of $X$ with $t$ for different values of $p=b/a$, and two sets of diagrams are given corresponding with the case where the volume of the resultants is 2/3 and 1/3 respectively of the volume of the reactants. This volume change is expressed in the general equation for the velocity by means of a quantity $\alpha$, in terms of which, if $B$ is present in excess, $v=v_0\{3a(1+\alpha X)+(b-a)\}/3a+(b-a)$, and if $A$ is present in excess, $v=v_0\{3b(1+\alpha X)+2(a-b)\}/3b+2(a-b)$. H. M. D.

**Periodic System of the Elements.** P. V. Wells (*J. Washington Acad. Sci.*, 1918, **8**, 232—234).—The author has redrawn the spiral periodic table of Stoney and others as revised by Harkins and Hall, and has given it a period of 8 instead of 16. The distance from the centre of the spiral to an element represents the atomic weight, and the elements are arranged in angular order of atomic number, each group being placed radially with the sub-groups slightly displaced. The metals of positive valence are sharply separated from the non-metals of negative valence. The proposed arrangement is much simpler than the double helix and has all its advantages; it overcomes the artificiality of the 16-period table and brings the main groups and sub-groups together. The new table is particularly adapted to illustrating the electron theory. The possibility of two forms of neon is indicated. A. B. S.

**Characteristic Frequency and Atomic Number.** H. Stanley Allen (*Proc. Roy. Soc.*, 1917, [*A*], **94**, 100—111. Compare this vol., ii, 14, 15, 163).—The relation between the atomic number and the characteristic frequency of an element is considered with reference to the theory of probability, and it is shown that the chance of the relation being accidental is very small.

According to Rydberg, there are two unknown elements between hydrogen and lithium, and the atomic number of lithium should be taken as 5 instead of 3, which is the value assigned by Moseley. The relation $N\nu = n\nu_A$ fits the results of observation more closely, however, when Moseley's numbers are used for $N$. With regard to the physical significance of the relation, it is supposed that the energy of the nucleus is an integral multiple of a certain quantity of energy characteristic of that condition of the atomic system which corresponds with the limiting frequency.

The similar relation connecting the atomic number and the electronic frequency is supposed to indicate that in the limiting conditions which are associated with the maximum of the photoelectric effect, the ionisation potential, and the thermionic potential we are dealing with a minimum value of the energy of the atomic system. H. M. D.

**Molecular Frequency and Molecular Number. II. The Frequency of the Longer Residual Rays.** H. Stanley Allen (*Phil. Mag.*, 1918, [vi], **35**, 404—409. Compare this vol., ii, 14, 163).—According to the results previously communicated, it would seem that the product of atomic number and atomic frequency in the case of an element, or of molecular number and molecular frequency in the case of a compound, is an integral multiple of a fundamental frequency which is approximately equal to $21 \times 10^{12}$ sec.$^{-1}$ In order to obtain the frequency of vibration of the atoms in compounds, recourse may be had to the residual rays which are obtained by repeated reflections from the surfaces of solids, and have been investigated by Rubens (compare A., 1910, ii, 172; 1913, ii, 648; 1914, ii, 236). By reference to the available data for the wave-lengths of the residual rays for various inorganic compounds, further evidence is obtained in support of the above relation between the molecular number and the molecular frequency.

The results obtained in this and the preceding papers suggest that the forces binding the atoms in the molecule are similar in character to those which bind the molecules of a solid. To account for the integral relations, it must be assumed that there is something of a discrete character in the nature of these forces, and the suggestion is made that the linkings between the atoms are constituted by Faraday tubes of force, which would then be regarded as physical entities. H. M. D.

**Device for Preventing Back-flow in Water Pumps.** MESTREZAT (*Ann. Chim. anal.*, 1918, **23**, 84—85).—An ordinary bicycle valve suitably fitted in the pipe connecting the pump with the vessel from which the air is to be exhausted prevents water passing into the latter. W. P. S.

**Modification of the Soxhlet Extractor.** J. W. WEIR (*J. Lab. and Clin. Med., St. Louis*, 1917, **3**, 204; from *Physiol. Abstr.*, 1918, **3**, 4).—A modification for use in the extraction of liquids is described and figured in the original. W. G.

**New and Simple Ultra-filters.** WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1918, **22**, 72—76).—Ultra-filters of simple construction for the filtration of colloidal solutions are described. It has been found that an efficient apparatus may be obtained by the use of either an ordinary or a Büchner funnel and filter paper which has been treated in situ with a 2% collodion solution. The best results were obtained, however, by the use of a Schleicher and Schüll Filtrierhut M 577 treated in the same way with the colloidal solution. The results obtained by subjecting a number of colloidal solutions of different kinds to ultra-filtration in this apparatus are described. H. M. D.

## Inorganic Chemistry.

**Recovery of Iodine from Dilute Residues.** HERBERT F. STEPHENSON (*Analyst*, 1918, **43**, 165—166).—The iodine is precipitated as mercuric iodide by treating the neutral or slightly acid liquid with mercuric chloride; when a suitable quantity of the iodide has been collected, it is treated at about 45° with a mixture of nitric and hydrochloric acids (1:5), then cooled, and the liberated iodine collected. Four parts of the moist iodine are now added in small quantities to a mixture of 1 part of iron filings and 10 parts of water; the mixture is boiled subsequently, treated with a slight excess of potassium hydroxide, the precipitated ferric hydroxide is separated, and the potassium iodide recovered by evaporating the solution. [See, further, *J. Soc. Chem. Ind.*, June.] W. P. S.

**A Third Kind of Sulphur Molecule. V.** A. H. W. Aten (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 824—830. Compare A., 1915, ii, 254).—Equilibrium between the two forms of sulphur, $S_\lambda$ and $S_\pi$, is attained less rapidly in toluene than in sulphur chloride. At 140°, six hours are required in the case of toluene, whereas equilibrium is reached in a few minutes in sulphur chloride solution.

Solutions of sulphur in toluene, in which equilibrium between $S_\lambda$ and $S_\pi$ had been established by heating at 140°, 150°, and 160°, were cooled to 0° and stirred for an hour in contact with rhombic sulphur; the sulphur content of the resulting solution was then determined, and from the results the proportions of $S_\lambda$ and $S_\pi$ in the solutions examined are derived. The proportion of $S_\pi$ increases with the temperature and also slightly with the concentration. Under similar conditions, the proportion of $S_\pi$ is considerably smaller in toluene than in sulphur chloride, but is approximately the same when toluene and carbon disulphide are used as solvents. H. M. D.

**Selenic Acid and Iron. Reduction of Selenic Acid by Nascent Hydrogen and Hydrogen Sulphide. Preparation of Ferrous Selenate and Double Selenates of the Iron Group.** A. E. H. Tutton (*Proc. Roy. Soc.*, 1918, [*A*], **94**, 352—361).—In an attempt to prepare ferrous selenate by the action of metallic iron on a solution of selenic acid, it was found that the iron becomes covered with a film of selenium which greatly retards the reaction and renders this method practically useless. No hydrogen is evolved, and the formation of the selenium would appear to be due to the reducing action of nascent hydrogen on the selenic acid, $6H + H_2SeO_4 = Se + 4H_2O$. The net result of such slow action as occurs may therefore be represented by the equation $3Fe + 4H_2SeO_4 = 3FeSeO_4 + Se + 4H_2O$. When the iron is replaced by zinc, hydrogen is given off, and very little reduction of selenic acid occurs. In the case of magnesium, hydrogen is also evolved, but reduction takes place to a considerable extent.

The reaction between ferrous carbonate (in the form of chalybite) and selenic acid also occurs very slowly, and for this reason cannot be used for the preparation of ferrous selenate. Solutions of this substance were readily obtained, however, by the action of ferrous sulphide on a concentrated solution of selenic acid. The hydrogen sulphide liberated in the primary reaction reduces the selenic acid to some extent in accordance with the equation $3H_2S + H_2SeO_4 = Se + 3S + 4H_2O$, but this does not interfere with the application of the method. If the filtered solution is allowed to crystallise, monoclinic crystals of $FeSeO_4,7H_2O$ isomorphous with $FeSO_4,7H_2O$ are obtained. The crystals of the selenate are much less stable than those of ferrous sulphate, and become opaque with such rapidity that it has not been possible to make any accurate goniometric observations with them.

The double selenates of the type $M_2SeO_4,FeSeO_4,6H_2O$ are readily obtained in the case of rubidium, cæsium, and ammonium. The corresponding potassium double selenate crystallises out if the temperature is not much higher than 0°. At the ordinary temperature, very small, monoclinic crystals of the dihydrated salt separate out. H. M. D.

**Telluric Acid and its Alkali Salts in their Behaviour as Semi-colloids.** ARTHUR ROSENHEIM and GERHART JANDER (*Kolloid Zeitsch.*, 1918, **22**, 23—44).—The investigation of telluric acid and its alkali salts has shown that these readily undergo polymerisation, with the formation of substances of semi-colloidal or colloidal character, according to the degree of polymerisation.

Measurements of the hydrogen ion concentration of $1N$-telluric acid solution gave $[H^{\cdot}]=4\times10^{-5}$ gram ion per litre. On the assumption that the acid ionises in accordance with the equation $H_6TeO_6=H^{\cdot}+H_5TeO_6{}'$, this gives $K=1{\cdot}6\times10^{-4}$ for the ionisation constant. According to this result, telluric acid is a very weak acid, approximating very closely to boric acid and hydrocyanic acid. This is in agreement with the very small value of the molecular conductivity, which increases from 0·1902 for $v=4$ to 0·6913 for $v=1024$ litres per gram molecule.

Freezing-point and boiling-point measurements for telluric acid solutions were also made, and these observations are in general agreement with the evidence afforded by the electrical measurements. Irregularities in the boiling points were found which are attributed to the formation of modifications of telluric acid of colloidal character. That the constitution of the aqueous solutions changes with rise of temperature is shown by the abnormally large value of the temperature coefficient of the molecular conductivity. The facts suggest that the more complex modification formed as the temperature rises is more strongly ionised than the modification which is represented by the crystalline acid. The so-called *allo*telluric acid described by Mylius (A., 1901, ii, 550) represents such a polymerised modification of greater conductivity. When aqueous solutions of *allo*telluric acid are kept at 25°, the conductivity falls, and ultimately reaches the value which is characteristic of the crystallised acid. The depolymerisation is also shown in other properties of the solution, but the milky appearance indicates that small quantities of a colloidal, insoluble modification are present. In view of this behaviour, it would seem that *allo*telluric acid is not a homogeneous modification, but consists of a mixture of polymerised forms differing considerably in complexity.

The investigation of the sodium, lithium, and potassium salts has shown that these behave in many ways like the free acid. These salts have no definite solubility in water; the quantity of water which the crystals contain varies according to the concentration of the solutions from which they are deposited, and the crystals undergo dehydration without any appreciable change in appearance. In these and other respects the salts resemble colloids. They not only absorb water, but experiments made with lithium tellurate show that the basic salts which have been described are in all probability adsorption compounds formed by the adsorption of lithium hydroxide from the solution. In a similar way, experiments made with potassium tellurate indicate that the so-called acid salts are adsorption compounds containing variable proportions of adsorbed telluric acid. In view of these observations, the statements made with respect to the alkali tellurates in the older literature must be accepted with reserve.

In the course of this investigation, solutions containing telluric acid and potassium nitrate was found to deposit large crystals of the composition $2KNO_3,H_6TeO_6,2H_2O$. This substance can be re-crystallised from dilute solutions of potassium nitrate without decomposition. With silver nitrate, the acid forms the compound $AgNO_3,H_6TeO_6$.

Reference is made to the fact that telluric acid readily crystallises with other salts, for example, with phosphates, arsenates, iodates, and oxalates. The formation of these additive compounds is supposed to be connected with the weak acid nature of telluric acid. H. M. D.

**Recent Studies on Active Nitrogen.** (Hon.) Robert John Strutt (T., 1918, **113**, 200—209).—A lecture delivered before the Chemical Society on February 21st, 1918. H. M. D.

**Nitride Formation.** E. B. Maxted (*J. Soc. Chem. Ind.*, 1918, **37**, 105—109).—The available data for the influence of temperature on the specific heats of nitrogen, hydrogen, and ammonia lead to the conclusion that the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$ will be displaced with rise of temperature in favour of the elementary gases, but that the proportion of ammonia will reach a minimum at a certain temperature and at higher temperatures will increase as the temperature rises. With the object of testing this result, which depends on an extrapolation of the formulæ connecting the specific heats of the gases with the temperature, the author has investigated the formation of ammonia at high temperatures by rapidly cooling the hot gaseous mixtures.

In one of the methods employed, the mixture of nitrogen and hydrogen was injected into an oxy-hydrogen flame burning under water, the ammonia contained in the water at the end of the experiment being estimated colorimetrically or by direct titration. The proportion of the injected mixture of nitrogen and hydrogen was varied in different experiments, resulting in changes in the flame temperature which could be approximately estimated. From the quantities of ammonia actually found in the several experiments, the author calculates the amount which would have been formed if the gas mixture consisted entirely of nitrogen, hydrogen, and ammonia at atmospheric pressure. In this way, it has been found that the proportion of ammonia increases from 0·0027 vol. % at 1280° (abs.) to 1·23 vol. % at 2580° (abs.).

In other experiments, the flame was cooled by contact with a water-cooled quartz tube. Under these conditions, the cooling is less rapid, and although these experiments show also that the equilibrium proportion of ammonia increases rapidly with the temperature, the quantities obtained were less than those in which the hot gaseous mixture was directly cooled by water.

The possibility of obtaining iron nitride by direct combination of nitrogen with the finely divided metal has also been examined. Although iron nitride begins to give off nitrogen at about 500° and decomposes rapidly at 600°, experiments in which finely divided iron was subjected to the action of nitrogen at 100 atmospheres between 500° and 700° showed no evidence of the formation of nitride. In view of this negative result, attempts were then made to determine the dissociation pressure of iron nitride. The nitride was slowly raised in temperature to 600°, and then allowed to cool slowly, the pressure being read off at various temperatures. Experiments were made for various initial nitrogen pressures, and although in all cases decomposition of the nitride took place at 600°, there was no evidence of recombination during the cooling process. In other words, equilibrium conditions are not realisable. The results obtained, however, suffice to show that iron nitride cannot be synthesised under the conditions obtaining in these experiments. H. M. D.

**The Production of Nitric Acid from Nitrogen Oxides.** Guy B. Taylor, Julian H. Capps, and A. S. Coolidge (*J. Ind. Eng. Chem.*, 1918, **10**, 270—275).—If a mixture of nitric oxide with excess of air from an oxidising plant is cooled and allowed sufficient time to oxidise to nitrogen peroxide, it will react with sulphuric acid in accordance with the equation $2NO_2+H_2SO_4=HNO_3+HNOSO_4$, and on electrolysis of the nitrososulphuric acid, the following reaction may take place: $HNOSO_4+2H_2O=HNO_3+H_2SO_4+H_2+2$ farads. In practice, however, the process is only efficient at first, since nitric acid or nitrososulphuric acid diffuses through the diaphragm and is reduced to nitric oxide with some free nitrogen. The chemical reactions involved in the conversion of nitric oxide to nitric acid in the arc and ammonia oxidation processes are:

(1) $2NO+O_2 \rightleftharpoons 2NO_2$.
(2) $2NO_2+H_2O \rightleftharpoons HNO_3+HNO_2$.
(3) $3HNO_2 \rightleftharpoons HNO_3+2NO+H_2O$.

Of these reactions, the first is the controlling one, and for this reason as much space as practicable should be allowed for the reaction in the plant. This reaction begins to proceed from left to right as soon as the gases have cooled below 600°, but is not complete even in the presence of a large excess of oxygen until the temperature reaches 200°. Since the reaction has a negative temperature coefficient, it is necessary to cool the gases as much as possible before entering the absorption system. [See also *J. Soc. Chem. Ind.*, June.] C. A. M.

**Amount of Phosphoric Acid in the Sea-water off Plymouth Sound.** DONALD J. MATTHEWS (*Reprint: J. Marine Biol. Assoc. United Kingdom*, 1917, **11**, 251—257. Compare A., 1916, ii, 635).—The amount of phosphoric acid in sea-water off Plymouth reached a maximum (0·06 mg. of $P_2O_5$ per litre) in December, 1915; it then decreased irregularly to a minimum (less than 0·01 mg. per litre) in April—May, 1916, and again attained the same maximum as before in January, 1917. This seasonal variation is probably due to the removal of phosphates from solution by algæ, diatoms, etc. W. P. S.

**The Fundamental Polyhedron of the Diamond Lattice.** ELLIOT Q. ADAMS (*J. Washington Acad. Sci.*, 1918, **8**, 240).—The author has found that the convex polyhedron with a symmetry corresponding with the point-system of the diamond space-lattice is the dodecatetrahedron *k*(111),(110). The arrangement of this in space constitutes a kind of twinning, which explains the fact that diamond is crystallographically holohedral, but the unit polyhedra are hemihedral. A. B. S.

**Oxidisable Constituents of Coal. I.** J. I. GRAHAM and J. HILL (*Trans. N. Eng. Inst. Min. Eng.*, 1918, **68**, 37—54).—Coal from the Barnsley soft seam was extracted with pyridine at 40° and 60 mm. pressure in an atmosphere of nitrogen. This was intended to prevent or minimise the absorption of oxygen and pyridine by the coal, which probably occurred in previous experiments on the extraction of coal with solvents. Ten to fifteen % of extract was obtained. The capacity for absorbing oxygen was determined for the extract, the residue, and the original coal by Winmill's method at 30° and 90°, both in air and an atmosphere of 90% oxygen. The absorption by the extract was negligibly small, whilst the avidity of the residue for oxygen was almost equal to that of the original coal. The humic and not the resinic constituent of this coal is the one responsible for tendency to spontaneous combustion. The extract, unlike those described by Wheeler (T., 1913, **103**, 1713), was inert towards a photographic plate, whilst the residue showed a great activity, not, however, due to the oxidation. [See, further, *J. Soc. Chem. Ind.*, 262A.] H. J. H.

**Carbonation. II. Carbonation of Distilled Water.** H. E. PATTEN and G. H. MAINS (*J. Ind. Eng. Chem.*, 1918, **10**, 279—288).—The rate of evolution of carbon dioxide from distilled water impregnated with carbon dioxide under pressure at 0° was measured by opening the bottle momentarily and noting the time required until the initial pressure was again shown on the pressure gauge. In this way, a series of simultaneous measurements of pressures and times was obtained, and from these data "pressure recovery" curves were constructed, in which the time in minutes represented the abscissæ and the pressure in lb. per square inch in excess of atmospheric pressure formed the ordinates. With the exception of the first curve corresponding with the first opening, in which an excessive quantity of gas was withdrawn, the curves showed a striking regularity, and were, in general, of a logarithmic type. The anticipated sudden rise of curve and sharp decrease of pressure were not observed. The results indicated that at a high pressure of carbon dioxide there is a close agreement with Henry's law. [See also *J. Soc. Chem. Ind.*, June.] C. A. M.

**Theoretical and Experimental Investigations on Metallic Alloys.** N. Parravano (*Ann. Chim. Applicata*, 1918, **9**, 1—86).—The author brings together the results of investigations on binary, ternary, and quaternary alloys made by himself and his collaborators and by De Cesaris, and already published in a series of thirty-seven papers during the years 1910—1917. T. H. P.

**The Stability of Dakin's Sodium Hypochlorite Solution.** Fritz Wischo and Franz Freiberger (*Münch. med. Woch.*, 1917, **64**, 1528—1529; from *Chem. Zentr.*, 1918, i, 228).—Concentrated Dakin solutions deteriorate to the extent of about 40% of the sodium hypochlorite in a month; they are comparatively stable when the amount of hypochlorite is reduced to 12·5%, but dilute solutions will keep better still, the decomposition being only about 10% in two months. J. C. W.

**The Double Sulphate of Sodium and Ammonium.** C. Matignon and F. Meyer (*Compt. rend.*, 1918, **166**, 686—688).—The heat of solution of the double sulphate,

$$Na_2SO_4,(NH_4)_2SO_4,4H_2O,$$

at about 15° is $-13{\cdot}00$ Cal., from which the following heats of formation of the double salt may be deduced:

$$(NH_4)_2SO_4 \text{ sol.} + Na_2SO_4 \text{ sol.} + 4H_2O \text{ liq.} = Na_2SO_4,(NH_4)_2SO_4,4H_2O \text{ sol.} + 11{\cdot}04 \text{ Cal.}$$

$$(NH_4)_2SO_4 \text{ sol.} + Na_2SO_4 \text{ sol.} + 4H_2O \text{ liq.} = Na_2SO_4,(NH_4)_2SO_4,4H_2O \text{ sol.} + 5{\cdot}54 \text{ Cal.}$$

$$(NH_4)_2SO_4 \text{ sol.} + Na_2SO_4,10H_2O \text{ sol.} = Na_2SO_4,(NH_4)_2SO_4,4H_2O \text{ sol.} + 6H_2O \text{ liq.} - 7{\cdot}6 \text{ Cal.}$$

The double salt is stable in the presence of its saturated solution between the temperature limits of 20° and 42°, and thus the salt may be prepared by evaporating a solution containing equimolecular proportions of the two generating salts between these temperatures. W. G.

**Crystals of Barium Disilicate in Optical Glass.** N. L. Bowen (*J. Washington Acad. Sci.*, 1918, **8**, 265—268).—Colourless, six-sided crystal plates with opaque white rims, which form in optical glass rich in barium have been identified with crystals of $BaSi_2O_5$ prepared synthetically. The white outlines are due to minute crystals which lie along the edges of the larger ones. A small amount of alkali disilicate appears to be contained in solid solution in the crystals in the glass. The plates are orthorhombic crystals with terminal angles 100°, lateral angles 130°, good cleavage parallel to elongation, negative elongation and optical character with $2V=70°$, refractive indices, $\gamma=1{\cdot}617$, $\alpha=1{\cdot}598$ in synthetic crystals, slightly lower in crystals in glass, isomorphous with $K_2Si_2O_5$. A. B. S.

**The Ternary System, $MgO$-$Al_2O_3$-$SiO_2$.** G. A. RANKIN and H. E. MERWIN (*Amer. J. Sci.*, 1918, [iv], **45**, 301—325).—The ternary system, magnesia–alumina–silica, has been investigated thermally to determine the melting temperatures of the various phases and microscopically to identify the various crystalline substances produced. The various boundary curves of the phases have been determined and the quintuple points fixed. It is shown that the following crystalline substances are stable in contact with the liquid phase: periclase ($MgO$), corundum ($Al_2O_3$), tridymite ($SiO_2$), forsterite ($2MgO,SiO_2$), clinoenstatite ($MgO,SiO_2$), spinel ($MgO,Al_2O_3$), sillimanite ($Al_2O_3,SiO_2$), and a ternary silicate, $2MgO,2Al_2O_3,5SiO_2$, which may be regarded as an end member in the cordierite series. The last compound is unstable at its melting point, and is considerably affected by solid solution. It has been observed in two forms; the $\mu$-form (unstable) crystallises from glass at temperatures below 950°, and is transformed at a somewhat higher temperature into the stable ($\alpha$) form. The properties of both forms, but more especially those of the $\alpha$-form, are very like those of the mineral cordierite. Seven quintuple points have been established, two of which are eutectics. The first lies at 1345°±5°, and is for $MgO,SiO_2$, $SiO_2$ and the ternary compound; the second lies at 1425°±5°, and is for $SiO_2$–$Al_2O_3,SiO_2$ and the ternary compound. The third point lies at 1460°±5°, and is for $Al_2O_3,SiO_2$–$MgO,Al_2O_3$ and the ternary compound; the fourth point lies at 1370°±5°, and is for spinel—$2MgO,SiO_2$ and the ternary compound. Point five lies at 1360°±5°, and is for $2MgO,SiO_2$–$MgO,SiO_2$ and the ternary compound. The sixth quintuple point is the eutectic point for $2MgO,SiO_2$–$MgO$ and spinel. It has a melting point 1700°±25°. The last point lies at 1575°±5°, and is for $Al_2O_3$, spinel, and $Al_2O_3,SiO_2$. The whole of the experiments were carried out either in a platinum resistance furnace for temperatures below 1600° or in an iridium furnace for higher temperatures. Diagrams and solid models of the system are given to illustrate the equilibria. J. F. S.

**Influence of Cadmium on the Properties of Alloys of Copper and Zinc.** LÉON GUILLET (*Compt. rend.*, 1918, **166**, 735—737).—A study of the effect of introducing from 0—4% of cadmium into brasses containing 60% or 70% copper on the mechanical properties of the alloy. Values are tabulated for the traction, shock, and hardness constants of the alloys, and notes on their micro-structure are given. [See, further, *J. Soc. Chem. Ind.*, June.] W. G.

**Colloidal Arsenates.** G. KLEMP and J. VON GYULAY (*Kolloid Zeitsch.*, 1918, **22**, 57—68. Compare A., 1915, ii, 256).—If solutions of potassium dihydrogen arsenate and zinc sulphate of appropriate concentration are brought together, there is no precipitation, but a jelly containing zinc hydrogen arsenate is formed. The same result is obtained if the zinc sulphate solution is mixed with solutions of disodium hydrogen arsenate or trisodium arsenate which have been previously neutralised by the addition of hydrochloric or acetic acid. When the jellies are kept for two or three months, crystals begin to separate. The crystals which separate from the jellies prepared from trisodium arsenate neutralised by acetic acid have the composition

$$Zn_3(AsO_4)_2,2ZnHAsO_4,4H_2O,$$

whilst those separating from the jellies prepared from potassium dihydrogen arsenate or from trisodium arsenate neutralised by hydrochloric acid consist of zinc hydrogen arsenate, $ZnHAsO_4,H_2O$. H. M. D.

**Sub-bromide and Sub-chloride of Lead.** HENRY GEORGE DENHAM (T., 1918, **113**, 249—256).—The method previously described for the preparation of lead sub-iodide (T., 1917, **111**, 29) has been extended to the corresponding bromine and chlorine compounds, the sub-bromide being obtained by the action of ethyl bromide vapour on lead sub-oxide at 261°, and the sub-chloride by the action of ethyl chloride on the sub-oxide at 311°. The two sub-compounds are grey in colour, fairly stable in the air, but are readily oxidised by bromine water or by permanganate solution. They are readily decomposed by acids with the formation of the normal salts and the metal.

The sub-salts are sparingly soluble in water. On the assumption that the salts are completely ionised and that the ions have the same mobility as those of the normal salts, the electrical conductivities of the saturated solutions give 2·2 milli-equivalents per litre for the solubility of the sub-chloride and 0·4 milli-equivalent for that of the sub-bromide. H. M. D.

**The Rare Earths. V. Holmium and Dysprosium.** H. C. KREMERS and C. W. BALKE (*J. Amer. Chem. Soc.*, 1918, **40**, 593—598. Compare A., 1917, ii, 259, and following abstract).—The concentration of dysprosium and holmium in a mixture of the yttrium earths, and the separation of holmium from yttrium have been studied. It is found that the fractionation of the bromates of the yttrium earths effects a rapid and efficient concentration of dysprosium and holmium. Starting with 12 kilos. of rare earth oxalates from gadolinite, which were converted into bromates, three parallel series of fifty recrystallisations were carried out. The series showed a concentration of samarium, neodymium, and praseodymium toward the insoluble end, dysprosium and holmium in the central portion, and yttrium, thulium, and erbium toward the soluble end. At this point, the material rich in dysprosium and holmium was removed from the three series, combined, and made into three new series, *A*, *B*, and *C*. Series *A* consisted of the more soluble fractions, and contained dysprosium, holmium, erbium, and yttrium. Series *B* contained the fractions richest in holmium and dysprosium, with small amounts of neodymium, praseodymium, erbium, and yttrium. Series *C* was composed of the less soluble bromates, and contained holmium, dysprosium, terbium, neodymium, praseodymium, and traces of erbium and yttrium. The three series were fractionated in parallel. The concentration of the earths in the different series was controlled mainly by the colour of the solutions. As the holmium and dysprosium became concentrated toward the less soluble end of series *A*, these fractions were added to series *B*, placing them where the fractions showed a similar colour. From series *C*, the more soluble dysprosium and holmium were removed and added to series *B* in the same way. In the same manner, yttrium and erbium which collected in the soluble end of series *B* were added to series *A*, and the neodymium and praseodymium from the less soluble end of *B* were placed in *C*. The three series were recrystallised thirty times, which caused most of the dysprosium and holmium to collect in series *B*; was eventually given a further sixty recrystallisations, which caused the holmium and dysprosium to concentrate very rapidly. A difficulty was experienced due to the repeated separation of cerium basic bromate as a brown sludge. It is therefore recommended that the cerium be removed by the sodium sulphate method before the fractionation commences. The separation of holmium from yttrium was also studied (i) by fractional precipitation with lactic acid, (ii) by fractional precipitation with ammonium carbonate, and (iii) by fusion of the nitrates. The first two methods were entirely unsuccessful. The fusion of a mixture of samarium, yttrium, and holmium nitrates gave a rapid concentration of the holmium. A mixture which had an equivalent of 98·6 at the start gave after thirty-one fusions four end fractions with equivalents 154·2—155·3. Attempts to separate holmium and yttrium by this method failed, and it was only after the addition of samarium that the separation became possible. J. F. S.

**The Rare Earths. VI. Purification and Atomic Weight of Dysprosium.** H. C. KREMERS, B. S. HOPKINS, and E. W. ENGLE (*J. Amer. Chem. Soc.*, 1918, **40**, 598—611. Compare A., 1917, ii, 259, and preceding abstract).—A short history of the knowledge of the element dysprosium is given in the paper. A quantity of dysprosium material of a high state of purity was further fractionated as ethyl sulphates and as bromates. It is shown that the ethyl sulphates are more efficient for the separation of dysprosium from neodymium, praseodymium, and terbium, and that neither of the methods is efficient for the separation of holmium from dysprosium. The atomic weight of dysprosium has been determined from the ratios (i) dysprosium sulphate to dysprosium oxide, (ii) dysprosium oxide to dysprosium chloride, and (iii) dysprosium chloride to silver. It is shown that the octahydrate of dysprosium sulphate is not constant in composition when dried over sulphuric acid, consequently the ratio $Dy_2(SO_4)_3,8H_2O : Dy_2O_3$ does not give trustworthy values for the atomic weight. The value Dy = 163·83 was obtained as the mean of nine experiments from the ratio $DyCl_3 : Dy_2O_3$, but since, on further investigation, it was shown that the oxide prepared for these experiments from the oxalate was not constant in composition, this value is rejected. By no method tried could an oxide be obtained which yielded concordant results from this ratio. Eight experiments were made to determine the ratio $DyCl_3 : 3Ag$, and the value 162·52 obtained. This is put forward as the most likely value, and is considerably lower than the result obtained (164·228) previously (*loc. cit.*). J. F. S.

**Determination of the Velocities of Cooling necessary to realise the Tempering of Carbon Steels.** P. CHEVENARD (*Compt. rend.*, 1918, **166**, 682—685).—A continuation of previous work (compare A., 1917, ii, 414). Using the method previously described (*loc. cit.*), and working with steels containing from 0·2—0·8% carbon, the author has determined, for different temperatures of heating, in the diagram plotting carbon content against velocity of cooling, the curves which mark the limit of appearance of martensite. The results indicate that, from the point of view of the effectiveness of tempering, an insufficient velocity of cooling can, to a certain extent, be compensated by an elevation of the temperature of heating. This compensation is less adequate as the carbon content of the steel diminishes. [See, further, *J. Soc. Chem. Ind.*, June.] W. G.

**The Reduction of Osmium Tetroxide by Hydrogen Chloride.** JAROSLAV MILBAUER (*J. pr. Chem.*, 1917, [ii], **96**, 187—189).—During experiments the results of which indicated that the chlorides of most metals are without appreciable influence on the rate of oxidation of aqueous hydrogen chloride by free oxygen or air, it has been found that, contrary to the general belief (compare Dammer, "Handbuch," III, p. 919), osmium tetroxide is reduced by concentrated hydrochloric acid with production of chlorine, the chemical change being representable by the equation $2OsO_4 + 12HCl = 2OsO + 6Cl_2 + 6H_2O$. D. F. T.

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## Mineralogical Chemistry.

**The Auriferous Minerals of the Côte d'Ivoire.** F. Roux (*Compt. rend.*, 1918, **166**, 645—646).—A sample of the metallic portion of a quartz, without visible gold, from Kokumbo gave on analysis: Au = 8·63%, Bi = 48·36%, Cu = 1·82%, Te = 37·52%, Ag = trace, S = 3·65%. Two metallic samples from the mineral at Poressou were each found to contain tellurium and bismuth.

W. G.

## Analytical Chemistry.

**Accurate Method for taking "Aliquots" in Volumetric Analysis.** Herbert E. Eastlack (*J. Amer. Chem. Soc.*, 1918, **40**, 620—622).—The author describes a method of taking aliquot parts of solutions for analysis, based on that of Miller (this vol., ii, 80), which is claimed to be simpler, more rapid, and more accurate than Miller's method. The newer method differs from the earlier one mainly in titrating the residue after the titrations have been made, instead of evaporating to dryness and weighing it.

J. F. S.

**Detection and Estimation of Bromine by Magenta-Sulphuric Acid Reagent.** G. Denigès and L. Chelle (*Ann. Chim. anal.*, 1918, **23**, 81—83).—The influence of nitrous acid on the detection of bromine by the magenta-sulphuric acid method described previously (A., 1913, ii, 72) may be prevented by carrying out the test at a temperature not exceeding 16°. Five c.c. of the bromide solution (containing not more than 1 gram of bromine per litre) are treated with 4 drops of concentrated hydrochloric acid, 4 drops of 10% potassium chromate solution, and 1 c.c. of concentrated sulphuric acid; the mixture is cooled at once to 15°, and 1 c.c. of the magenta reagent and 1 c.c. of chloroform are added; the chloroform is coloured red when the mixture is shaken, the intensity of the coloration depending on the quantity of bromine present.

W. P. S.

**New General Method for Determining Iodine in Inorganic and Organic Compounds.** N. Tarugi (*Gazzetta*, 1918, **48**, i, 1—16).—This method is based on the reaction $6FeSO_4 + 3H_2SO_4 + 2ICl_3 = 3Fe_2(SO_4)_3 + I_2 + 6HCl$. The iodine formed is extracted by means of chloroform and titrated with thiosulphate, whilst the chlorine is determined by titrating with permanganate the residual acid solution from the extraction, this containing the ferric sulphate and the excess of the ferrous sulphate. In this way, the proportions of iodine and chlorine, and thus those of iodine trichloride and monochloride in a solution of iodine trichloride, are obtained.

By simple methods, the iodine in an inorganic or organic compound may be converted into iodine trichloride and then estimated as above. [See, further, *J. Soc. Chem. Ind.*, 285A.] T. H. P.

**Oxidation of Sulphides with Potassium Iodate.** REGINALD S. DEAN (*J. Amer. Chem. Soc.*, 1918, **40**, 619—620).—In a previous paper (A., 1915, ii, 480), it was shown that in the estimation of sulphides by oxidation with potassium iodate in the presence of hydrochloric acid, the amount of sulphur oxidised to sulphuric acid depended on the concentration of the acid, and that with an amount of iodate equivalent to the sulphide, the maximum amount of oxidation is represented by the equation $3MS + 3KIO_3 + 12HCl \rightleftharpoons 3MCl_2 + 2S + H_2SO_4 + 3KCl + 3ICl + 5H_2O$. It is now shown that with an excess of iodate and hydrochloric acid of any strength sufficient to prevent the hydrolysis of the iodine chloride formed, the whole of the sulphur is quantitatively oxidised to sulphuric acid according to the equation $H_2S + 2KIO_3 + 4HCl \rightleftharpoons 2ICl + H_2SO_4 + 2H_2O + 2KCl$. The estimation is carried out as follows. A solution of hydrogen sulphide is treated with the requisite excess of potassium iodate solution and hydrochloric acid (6—3*N*), and the excess of iodate estimated by means of a standard iodine solution. The method has also been applied to the estimation of lead sulphide; the freshly precipitated lead sulphide is introduced into the iodate solution, hydrochloric acid added, and the titration completed as before. The results in both cases agree within 0·1% of the theoretical value. J. F. S.

**The Estimation of Thio-esters in Urine.** LUCIEN CORDIER (*J. Pharm. Chim.*, 1917, [vii], **16**, 360—363).—The author considers that Gauvin's method (A., 1914, ii, 142) of hydrolysis of the thio-esters by boiling the urine with one-fifth its volume of hydrochloric acid for fifteen minutes gives satisfactory results in the estimation of these constituents in urine. W. G.

**Two Methods of Destruction of Organic Substances in Urine.** LUCIEN CORDIER (*J. Pharm. Chim.*, 1917, [vii], **16**, 363—367).—In the first method, 20 c.c. of urine are evaporated to dryness with 4 grams of a mixture of equal parts of potassium nitrate, anhydrous potassium carbonate, and anhydrous sodium carbonate. The dry residue is intimately mixed with a further 8 grams of the fusion mixture and fused until all the carbon is oxidised. The second method is a modification of that of Gautier and Clausmann for animal tissues (compare A., 1917, ii, 421). Twenty c.c. of urine are evaporated to dryness with 2 grams of magnesium nitrate, and the dry residue is strongly heated until all the carbon is burnt off. The residue from either fusion may be used for the estimation of total sulphur in urine. W. G.

**Detection of Carbon Dioxide in the Analysis of Carbonates or Oxalates.** O. F. STAFFORD (*J. Amer. Chem. Soc.*, 1918, **40**, 622).—In order to detect the presence of carbon dioxide in the gaseous products of the action of acids on minerals, the author inserts a glass tube into the mouth of the test-tube; this tube is drawn out to a capillary fine enough to cause a drop of the reagent (baryta water) to remain in it, and not too fine to prevent bubbles of the gas being drawn upward through the liquid. To make the test, the gas from the test-tube is drawn through the baryta water by aspirating at the top of the inserted tube. The method may be made roughly quantitative for small traces of carbonates or oxalates. Two such capillaries are used; the material to be examined is placed in one, and the second tube, containing a drop of baryta water, inserted into the mouth of the first and sealed to it by means of "Khotinsky" cement. Then by aspirating a drop of 30% sulphuric acid is drawn on to the material, and the gas generated drawn through the baryta water. In the case of oxalates, 30% sulphuric acid mixed with potassium permanganate is used. The turbidity produced in the baryta water is compared with turbidities produced similarly from known amounts of carbonates or oxalates. J. F. S.

**Water Analysis in the Field.** GEORGE W. HEISE and A. S. BEHRMAN (*Philippine J. Sci.*, 1918, **13**, [A], 1—17).—The methods are based on those of Leighton [U.S. Geol. Survey, Water Supply Paper (1905) No. 151], and bacteriological examination is also made. Titrations are effected with reagents in pellet form. [See, further, *J. Soc. Chem. Ind.*, June.] H. J. H.

**Detection of Potassium by the Use of Light Filters.** ALOIS HERZOG (*Chem. Zeit.*, 1918, **42**, 145).—The light filter recommended is prepared by coating a glass plate with a gelatin solution containing a mixture of the two dyes patent blue and tartrazin in such proportion that each sq. metre of glass shall have on it 3·9 grams of the former and 2·5 grams of the latter dye. Viewed through this screen, the potassium flame appears bright red surrounded by a yellowish-green fringe. Rubidium is the only other element which gives a coloration similar to that shown by potassium. Green and violet dyes may be used for the purpose, but preference is given to the mixture mentioned.

W. P. S.

**Iodide Titration of Silver Nitrate with Palladous Nitrate as Indicator.** LOUIS SCHNEIDER (*J. Amer. Chem. Soc.*, 1918, **40**, 583—593).—The Volhard method for the volumetric estimation of silver is interfered with by the presence of certain metals and loses its sensitiveness for very dilute solutions. The author describes a method whereby silver solutions may be titrated with iodide in the presence of such metals and in very dilute solution by use of a solution of palladous nitrate as indicator. The indicator is prepared by dissolving 0·06% of palladous nitrate in 16% nitric acid; it is found advisable to use a protective colloid along with the indicator to prevent the occlusion of potassium iodide or silver nitrate. For this purpose, a 5% solution of gum arabic is found most advantageous. The indicator is converted by the first excess of iodide into palladous iodide, which gives a red colour to the solution; this action is sensitive to 1 part in 500,000. This method is further to be recommended on account of the accuracy and easy reproducibility with both *N*/10- and *N*/1000-solutions. The author discusses at some length the possible errors of the method, and gives full details of the procedure to be adopted for *N*/10- and *N*/1000-solutions. J. F. S.

**Field Methods for the Determination of the Total Hardness of Water.** A. S. BEHRMAN (*Philippine J. Sci.*, 1918, **13**, [A], 21—27).—Blacher's method of titration with potassium palmitate has been adapted to field conditions. The water is titrated with standard pellets of the reagent. [See, further, *J. Soc. Chem. Ind.*, June.] H. J. H.

**Analysis of Glass.** L. RONNET (*Ann. Falsif.*, 1918, **11**, 26—31).—A scheme is given for the analysis of glass containing silica, iron, aluminium, manganese, calcium, magnesium, potassium, and sodium. The usual methods of separating and estimating these constituents are employed. [See, further, *J. Soc. Chem. Ind.*, 1918, 266A.] W. P. S.

**Estimation of the Reducing Power of Urine, both free from and containing Dextrose, by means of an Alkaline Glycerol-Copper Solution.** H. RUOSS (*Zeitsch. physiol. Chem.*, 1918, **101**, 131—164).—The method previously described (A., 1917, ii, 549) is modified by employing a glycerol–copper solution and by using always the same volume of urine with varying quantities of copper solution instead of maintaining a constant volume of the latter and varying the former. The glycerol–copper solution is prepared by dissolving 3·464 grams of copper sulphate in 10 c.c. of hot water, cooling, and adding 15 c.c. of glycerol and 22 c.c. of sodium hydroxide solution (D 1·357). The mixture is again cooled, 5 c.c. of a 30% potassium thiocyanate solution added, and then the volume brought to 100 c.c. by the addition of 25% sodium chloride solution. For an estimation, 5 c.c. of urine are treated with from 0·1 to 1 c.c. of the new reagent, and, after boiling, the end-point determined in the manner previously described (*loc. cit.*). The amount of copper solution is varied until it is exactly reduced by the dextrose or other reducing substances present in the urine.

Attention is directed to the fact that the reducing power of urine free from sugar is proportional to $D-1$, where $D$ is the specific gravity of the urine, and that the urine may be freed from substances containing nitrogen by treatment with an excess of the Patein-Schöndorff mercuric nitrate reagent (A., 1908, ii, 311), the excess of mercury being subsequently removed by precipitation with alkali followed by zinc dust. H. W. B.

**Copper-Phosphate Mixtures as Sugar Reagents. A Qualitative Test and a Quantitative Titration Method for Dextrose in Urine.** OTTO FOLIN and W. S. MCELLROY (*J. Biol. Chem.*, 1918, **33**, 513—519).—The qualitative reagent is prepared by dissolving 100 grams of sodium pyrophosphate (U.S.P.), 30 grams of crystallised disodium hydrogen phosphate, and 50 grams of anhydrous sodium carbonate in about a litre of water, and adding 13 grams of copper sulphate previously dissolved in about 200 c.c. of water. The solution appears to keep indefinitely and is cheaply prepared. To test for reducing sugars, 5 c.c. of the reagent are placed in a test-tube, five to eight drops (not more than 0·5 c.c.) of the urine added, and the mixture boiled for one minute, or heated in boiling water for three to five minutes. Minute traces of sugar are indicated by various grades of turbidity, larger amounts by unmistakable precipitates of cuprous oxide. A slight turbidity occurring after cooling may be due only to the reducing action of normal urine.

For quantitative estimation, the only solution required is an acidified copper sulphate solution containing 60 grams of crystallised copper sulphate and 4 c.c. of concentrated sulphuric acid per litre. Five c.c. of this solution correspond with 25 mg. of dextrose or lævulose, 45 mg. of anhydrous maltose, or 40·4 mg. of anhydrous lactose. The other necessary reagent is a dry mixture containing 100 grams of crystallised disodium hydrogen phosphate, 60 grams of dry sodium carbonate, and 30 grams of sodium or potassium thiocyanate. The authors recommend the titrations to be made in test-tubes, using undiluted urine. This simplification is made possible by attaching to the tip of an ordinary 25 c.c. glass-stoppered burette another tip consisting of a glass tube drawn out at one end to an almost capillary bore, and delivering between forty-five and fifty-five drops of urine per c.c. If the burettes carrying accessory tips are filled by suction, the necessity of rinsing the burette with the sugar solution to be titrated is avoided, which can be proved by filling the burette with water after it has just been emptied from a urine containing 5% of sugar. On testing the water in the lower part of the burette, it is found to be quite free from sugar. To carry out an estimation, 5 c.c. of the copper reagent and 4 to 5 grams of the dry salt mixture are heated in a test-tube until a clear solution is obtained (a pebble is added to prevent bumping). Twenty-five drops of urine are run in from the burette, and the mixture gently boiled for two minutes. If the solution is still blue, more urine is run in, boiling for one minute after each addition, until the solution is colourless. From the total number of drops, the volume of urine added can be computed, and hence the percentage of dextrose in the urine. The results of the titration should be confirmed by a repetition, in which the first addition of urine should be only two or three drops less than the full amount of urine required. The total period of boiling must not be less than four or more than seven minutes.

The presence of albumin in the urine does not obscure the end-point of the titration. The use of the test-tube instead of a flask or beaker greatly retards the reoxidation of the cuprous oxide and materially aids the rapid performance of the test. If desired, a 5 c.c. burette graduated in 0·02 c.c. divisions may be used instead of the ordinary burette with capillary tip described above.

H. W. B.

**Estimation of Lactose in Milk.** Otto Folin and W. Denis (*J. Biol. Chem.*, 1918, **33**, 521—524).—The authors describe two methods, based on titration and colorimetry respectively, the former being considered to give the more nearly accurate results. In the titration method, the reagents and apparatus described for the estimation of dextrose in urine (preceding abstract) are employed, and neither the protein nor the fat is previously removed from the milk. The milk is simply diluted with water (1 : 4) and added directly to the copper–phosphate solution, boiling being continued rather longer than in the estimation of dextrose.

For the colorimetric estimation, a modification of Dehn and Hartman's method (A., 1914, ii, 223) is described which is based on the colour developed when an alkaline solution of lactose in saturated picric acid is heated for a fixed time at 100°. [See, further, *J. Soc. Chem. Ind.*, 278A.] H. W. B.

**Estimation of Dicyanodiamide in Old Calcium Cyanamide.** H. Kappen (*Zeitsch. angew. Chem.*, 1918, **31**, 31—32).—A sample of very old calcium cyanamide was found to be free from cyanamide nitrogen; the dicyanodiamide nitrogen was estimated by Caro's and by Hager's methods. The results obtained by these two methods did not agree (compare Hager and Kern, A., 1916, ii, 687), and the author suggests that the difference may be due, in part, to the presence of urea in the sample. This is confirmed by the results of analyses of mixtures of urea and dicyanodiamide; urea has less effect on the results obtained by Caro's method than it has on those found by Hager's method. W. P. S.

**The Spectroscopic-quantitative Estimation of Urochromogen.** Traugott Baumgärtel (*Biochem. Zeitsch.*, 1918, **85**, 162—170).—The author gives a modification of the method of Weiss for the estimation of urochromogen by oxidation with potassium permanganate, in which the colorimetric method adopted by Weiss is replaced by the detection of excess of permanganate spectroscopically. The method has been applied to the determination of the urochromogen output in the urine in certain pathological cases. S. B. S.

# General and Physical Chemistry.

**Double Refraction and Optical Activity of Liquid-Crystalline Substances.** FELIX STUMPF (*Jahr. Radioakt. Elektronik*, 1918, **15**, 1—64).—A useful and detailed résumé, including bibliography, of the work since the earlier résumé in the same journal by R. Schenck in 1909, is given in six chapters, entitled: (1) Double refraction of inactive and active substances. (2) Rotation of plane of polarisation. (3) Theory of uniaxial active absorbing crystals. (4) Observations on the state of polarisation oblique to the axis of the advancing waves. (5) The theory of M. Born and its experimental examination. (6) The action of the magnetic field on liquid-crystalline substances. F. S.

**Anomalous Molecular Distribution in Mixed Crystals as the Cause of their Anomalous Double Refraction.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 226—235; from *Chem. Zentr.*, 1918, i, 567).—A consideration as to the cause of the internal strains to which the anomalous optical properties of some mixed crystals have been attributed. It is not very probable that during rapid crystallisation correct distribution of the components can occur completely so that the blending is entirely consistent with the symmetry of the space lattice. The disturbance in the molecular distribution will cause a reduction in the linear velocity of crystallisation and a deviation in the properties of the mixed crystal from those expected from its symmetry; both these effects are frequently observed. If an anomalous mixed crystal represents an unstable system, the solubility should be least for the normal mixed crystal, as has, indeed, been observed. It is calculated that the alteration in solubility to be expected from the effect of the internal strains in a certain case is 0·3%, whereas the observed difference in solubility may attain 50%. According to this result, the abnormal arrangement in the crystal lattice exerts a direct influence, and not merely an indirect effect on account of the internal strains. D. F. T.

**Electrical Double Refraction in Liquids.** C. BERGHOLM (*Ann. Physik*, 1917, [iv], **54**, 511—518).—The author discusses the question of the dependence of the electrical double refraction on the composition and constitution of organic compounds, and points out that Kerr's constant cannot be considered to offer a suitable basis for the comparison of different substances. In place of Kerr's constant $B$, the quantity $B_R = B\lambda nM/(K+2)^2(n^2+2)^2d$ is proposed, $\lambda$ being the wave-length of the light used, $n$ the ordinary refractive index, $M$ the molecular weight of the substance, $K$ the dielectric constant, and $d$ its density. The quantity $54B_R$ represents the "electrical double refraction of the molecular refraction" for a layer of liquid 1 cm. in thickness and an electrostatic field of unit intensity. The values of $B_R$ for a number of substances are compared, and from this it would seem that in the case of aromatic compounds which have similar absorption spectra, the value of $B_R$ varies but little with the nature of the substituent element or group and its position in the benzene ring.

H. M. D.

**The Light Emission of Gases and Mixtures of Gases by Electric Discharges.** L. Hamburger (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1043—1048).—A summary is given of experiments in which the effect of pressure and of the intensity of the electric discharge on the emission spectra of certain gases and gas mixtures was examined.

The observations made with nitrogen, hydrogen, neon, and helium show that the intensity of the lines and bands is proportional to the energy of the discharge, and that the maximum emission is displaced towards the ultra-violet when the pressure is decreased. Argon behaves quite differently, and the nature of the divergence depends on whether the red or the blue spectrum is emitted. If the intensity is plotted against the strength of the current, curves are obtained which are concave or convex to the current axis, according to whether the red or the blue spectrum is considered.

Observations made on mixtures of non-reactive gases show that there is generally a shift of the maximum towards the ultra-violet which may be interpreted in terms of the pressure effect referred to above. In the case of mixtures of gases which react with each other, the observations show that new bands make their appearance in the discharge spectrum.

H. M. D.

**Absorption of Ultra-violet Rays by Phenyl Derivatives of Methane.** G. Massol and A. Faucon (*Compt. rend.*, 1918, **166**, 819—821).—A study of the absorption spectra of benzene, toluene, and di- and tri-phenylmethanes. The results indicate that benzene and the three phenyl derivatives of methane show a general transparency for the radiations extending from the visible spectrum to $\lambda=270$ and a selective absorption for the radiations from $\lambda=270$ to $\lambda=230$. This selective absorption varies with the different compounds, and the characteristic spectrum of benzene with its narrow bands and its undulating aspect is not found in the phenyl derivatives of methane. Their bands are less numerous, often slightly displaced, and do not all appear at the same time. The transparency diminishes as the molecular weight increases.

W. G.

**Confirmation of van't Hoff's Hypothesis. Optical Superposition in the Meta-saccharins and Related Substances.** Edwin A. Hill (*J. Amer. Chem. Soc.*, 1918, **40**, 764—773).—The question of the validity of the principle of optical superposition has been examined by reference to the rotatory powers of the four meta-saccharins and of their strychnine, brucine, and quinine salts. It is shown that the specific and molecular rotations may be satisfactorily represented as the algebraic sums of three constants corresponding with the active $\alpha$-, $\gamma$-, and $\delta$-carbon atoms. The calculated constants for the $\alpha$- and $\gamma$-carbon atoms are very nearly the same for all the salts, but differ considerably from the $\alpha$- and $\gamma$-constants for the saccharins themselves. This is quite in accordance with the fact that ring structure is present in the saccharins, whilst the salts are characterised by chain structure. The sum of the activities of the $\delta$-carbon atom and the active base remains constant for the four salts corresponding with each of the three bases, but changes its value with the nature of the alkaloid.

By using the average values of the constants and calculating the specific rotations of the twelve salts, it is found that the average differences between the calculated and observed rotations are 0·94° for the strychnine salts, 0·25° for the brucine salts, and 0·22° for the quinine salts.

Reference is made to other recorded data which afford evidence of the validity of the principle of optical superposition.

H. M. D.

**Action of Light-rays on Organic Compounds and the Photosynthesis of Organic from Inorganic Compounds in Presence of Inorganic Colloids.** BENJAMIN MOORE and T. A. WEBSTER (*Proc. Roy. Soc.*, 1918, [*B.*] **90**, 168—186).—In the formation of formaldehyde from carbon dioxide in light in the presence of an inorganic catalyst, it is shown that the action depends, not only on the specific character of the catalyst, but also on its state of aggregation. Exposure of formaldehyde solutions to light lead to the formation of condensation products which reduce Benedict's solution. The relationship between the osmotic energy and thermochemical relations in reversible reactions of this description is discussed. The authors also discuss generally the formation of formaldehyde by phytochemical decomposition of more complex substances. S. B. S.

**The Parent of Actinium.** FREDERICK SODDY and JOHN A. CRANSTON [and, in part, ADA HITCHINS] (*Proc. Roy. Soc.*, 1918, [*A.*] **94**, 384—404).—The history of the long search for the parent of actinium, and of the various theories that have been framed to connect it with uranium, is dealt with in full. The present work was undertaken to test the hypothesis that actinium is produced from "eka-tantalum," the missing element between uranium and thorium in the Periodic Table, by its disintegration in a slow $\alpha$-ray change, giving actinium. Eka-tantalum is probably the product of uranium-$Y$, discovered by Antonov (A., 1911, ii, 844; 1914, ii, 17), and it should be isotopic with uranium-$X_2$ or brevium.

It was found that uranium-$X_2$ could be effectively separated from uranium-$X_1$, isotopic with thorium, by distillation at a dull red heat in chlorine charged with carbon tetrachloride vapour, the uranium-$X_2$ volatilising. The attempt was made to separate eka-tantalum from pitchblende similarly. About 500 grams of a very pure Indian pitchblende ($U_3O_8$ 86%, PbO 11·9%, $ThO_2$ 1·9%, $SiO_2$ 0·6%) similarly treated gave three sublimates, the first after twenty-two hours, the second after ninety hours further, and the last [prepared by (Miss) A. Hitchins] after six hours at a much higher temperature. These sublimates were kept under observation for the growth of actinium, from which they were initially free. The presence of actinium was tested for by means of its characteristic active deposit. The second sublimate, in the course of one thousand days, produced a quantity of actinium twenty times greater than could be with certainty detected. So far as can yet be seen, the rate of growth of actinium appears to be linear with the time, pointing to a direct production. The other preparations have remained free from actinium. Another preparation, from Joachimsthal pitchblende, treated similarly, gave a sublimate also giving actinium with time. For the second sublimate from Indian pitchblende, the attempt was made to compare the quantity of actinium present after 2·5 years with that in the originating pitchblende. The amount of actinium present was found to be the same as that in 0·25 gram of the pitchblende. On the assumptions (1) that the actinium is produced in a direct change, (2) that the sublimate contained all the parent of actinium present in the original mineral, the period of average life of actinium is calculated to be 5,000 years. The quantitative measurement by radio-active methods of minute quantities of actinium by means of its emanation and active deposit presents difficulties which have not been completely overcome. The work supports the theory of the origin of actinium, referred to at the beginning, but does not finally establish it to the exclusion of all other possible modes of origin.

F. S.

**Mobilities of Ions in Air, Hydrogen, and Nitrogen.** Kia-Lok Yen (*Proc. Nat. Acad. Sci.*, 1918, **4**, 91—97).—The mobilities of the positive and negative ions in air, hydrogen, and nitrogen have been measured at various pressures and for widely different potentials. The results show that the mobility varies inversely as the pressure, and that the product of these quantities is independent of the strength of the field in the case of both positive and negative ions. The results are discussed with reference to the constitution of the ions, and the author contends that they afford support for the view that the ions consist of a single atom or molecule, as opposed to the cluster hypothesis according to which an ion is supposed to consist of a relatively large group of satellite molecules. The fact that the mobility of the negative ions is in all cases greater than that of the positive ions can be readily explained in terms of the simple ion hypothesis when the relative magnitude of the forces acting between neutral molecules and ions of opposite sign is taken into account. This attractive force is greater for the positive ion, and, in consequence, the effective mean free path of the positive ion is less than that of the negative ion.

The reduced mean free path involves a diminution in the mobility of the positive ions as compared with that of the negative ions.
H. M. D.

**Mobilities of Ions in Vapours.** KIA-LOK YEN (*Proc. Nat. Acad. Sci.*, 1918, **4**, 106—109).—The mobilities of the positive and negative ions in sulphur dioxide, acetaldehyde, ethyl chloride, ethyl alcohol, pentane, acetone, ethyl acetate, ethyl iodide, and methyl iodide have been measured at various pressures. The mean values obtained show that the mobility of the negative ion is slightly greater than that of the positive, except in the case of ethyl iodide, for which the observed values are the same. The ratio of the mobilities of the oppositely charged ions in these vapours is much smaller than the ratio found in the case of air, hydrogen, and nitrogen, and is quite in accordance with the assumption that the ions are simple in type (compare preceding abstract). H. M. D.

**The Distribution of Radioactive Gases in the Free Atmosphere.** VICTOR F. HESS and WILHELM SCHMIDT (*Physikal. Zeitsch.*, 1918, **19**, 109—113).—From the point of view of present knowledge of the interchange going on in the free air by virtue of the random molecular motion, the law for the distribution with height of a radioactive gas in the atmosphere and the comparison of the amount at any altitude with that present at the earth's surface have been worked out. The calculated values agree with such observations as have been made for the radium emanation, so far as the order of magnitude is concerned. The calculated values, for the height in which the quantity of the radioactive material per gram of air is reduced to half the value at the surface, are:

Radium emanation and its short-lived products, about 1200 metres.

Radium-*D* and subsequent products, uniform up to 10 kilometres.

Thorium emanation and thorium-*A*, 2 to 3 metres.

Thorium-*B* and subsequent products, 100 to 150 metres.

Actinium emanation and actinium-*A*, 0·5 to 1 metre.

Actinium-*B* and subsequent products, 10 to 20 metres.

The total quantity of radium emanation in the whole atmosphere is estimated as between 1·6 and $2·3 \times 10^7$ Curies. F. S.

**Attempted Separation of Isotopic Elements by means of Fractional Diffusion.** H. LACHS, M. NADRATOWSKA, and L. WERTENSTEIN (*Compt. rend., Soc. Sci. Warsaw*, 1917, **9**, 670—672; from *Chem. Zentr.*, 1918, i, 416).—In an attempt to separate the isotopes $U_1$ and $U_2$ by the fractional diffusion of a solution of uranyl nitrate, no difference was observable between the radioactivity of the diffusate and of the original substance. If there is any difference between the diffusion coefficients of the two isotopes, it cannot be greater than 1·5%. D. F. T.

**Can the Production of Electricity by Organic Substances and Living Tissue be Explained by known Thermodynamic Laws?** R. BEUTNER (*Zeitsch. Elektrochem.*, 1918, **24**, 94—100).—Polemical against Baur and Kronmann (A., 1917, ii, 231). It is shown that the production of the current in two-phase liquid elements can be explained thermodynamically, and, consequently, the production of the biological current can also be explained in the same way. It is claimed that the absorption theory of Baur, which is put forward to take the place of the thermodynamic theory, is therefore superfluous, and, furthermore, unproved. J. F. S.

**Can the Production of Electricity by Organic Substances and Living Tissues be Explained by known Thermodynamic Laws?** EMIL BAUR (*Zeitsch. Elektrochem.*, 1918, **24**, 100—101).—Polemical, an answer to Beutner (see preceding abstract). J. F. S.

**Potentials of the Bismuth-Bismuth Oxychloride and the Copper-Cuprous Chloride Electrodes.** ARTHUR A. NOYES and MING CHOW (*J. Amer. Chem. Soc.*, 1918, **40**, 739—763).—The normal potentials have been derived from measurements of the *E.M.F.* of cells formed by combination of the bismuth oxychloride and cuprous chloride electrodes with the hydrogen electrode and with each other. The mean values obtained for the normal potential of the bismuth oxychloride electrode are −0·1635, −0·1599, and −0·1563 volt at 15°, 25°, and 35° respectively. The corresponding values for the cuprous chloride electrode are −0·1263, −0·1200, and −0·1132 volt respectively.

From the temperature coefficients of the electrode potentials, the authors have calculated the heat changes accompanying the chemical reactions. The results are expressed in the equations

$$3/2H_2 + 3CuCl = 3Cu + 3\overset{+}{H} + 3\overset{-}{Cl} + 21570 \text{ cal.}$$

$$3/2H_2 + BiOCl = Bi + H_2O + \overset{+}{H} + \overset{-}{Cl} + 18500 \text{ cal.}$$

$$Bi + 3CuCl + H_2O = 3Cu + BiOCl + 2\overset{+}{H} + 2\overset{-}{Cl} + 2825 \text{ cal.}$$

By measuring directly the heat of the reaction between metallic tin and bismuth oxychloride, and also of the reaction between tin and cuprous chloride in presence of dilute hydrochloric acid, the value found for the last of the above reactions is 7390 cal., which is very much larger than that indicated by the potential measurements. The discrepancy has not yet been accounted for.

The equilibrium corresponding with the equation $Bi + 3CuCl + H_2O \rightleftharpoons 3Cu + BiOCl + 2\overset{+}{H} + 2\overset{-}{Cl}$ has been determined by experiments at 75°. The constant $K_{75} = [\overset{+}{H}]^2 . [\overset{-}{Cl}]^2$ has the value $2·10 \times 10^{-3}$. H. M. D.

**Electrical Endosmose. II.** T. R. BRIGGS, H. S. BENNETT, and H. L. PIERSON (*J. Physical Chem.*, 1918, **22**, 256—272. Compare A., 1917, ii, 236).—An improved form of electro-osmometer is described which consists essentially of a horizontal tube containing the diaphragm, in close proximity to which are the electrodes, which pass through vertical side tubes which permit of the escape of gases generated during the passage of the current. The anode and cathode compartments are also connected through a narrow tube which contains an air bubble. This tube is provided with a scale, and the rate at which the bubble moves along the tube affords a measure of the electro-endosmotic flow.

Measurements have been made which show the dependence of the effect on the applied potential difference, the temperature, and on the nature of the diaphragm and of the dissolved electrolyte.

The rate of endosmotic flow is proportional to the applied difference of potential. For a given potential, it increases with rise of temperature, the rate of increase being somewhat smaller than that of the fluidity.

The results obtained in the investigation of dilute acid and alkaline solutions confirm the observation, made by Perrin, that the direction of flow undergoes reversal on passing from an acid to an alkaline solution. With a carborundum diaphragm, the isoelectric point was found to correspond with a very slightly acid solution. Sharp reversals were also obtained with alundun and also with diaphragms of gelatin and agar jellies. With powdered glass, no reversal was obtained.

Observations made with various copper salts are also recorded, and the bearing of the electro-endosmotic effects on the electrical and adsorption theories of dyeing is discussed in reference to some experiments made with acid and basic dyes. H. M. D.

**The Abnormality of Strong Electrolytes. I. Electrical Conductivity of Aqueous Solutions.** JNANENDRA CHANDRA GHOSH (T., 1918, **113**, 449—458).—The fact that the ionisation of strong electrolytes, as measured by the electrical conductivity or osmotic methods, does not vary with the dilution in accordance with the requirements of the law of mass action, is supposed to be due to the invalidity of the fundamental idea underlying the Arrhenius ionic theory. According to the author, strong electrolytes are completely ionised, and there is no question of an equilibrium between ions and unionised molecules. The relations between the ions are determined solely by the electrical forces acting between the ions, and the interior of a solution of a strong electrolyte is characterised by a certain potential, $A$, which affords a measure of the work which is required to remove the ions from the influence of their mutual attractive forces. By application of the kinetic theory, it may be inferred that ions become "free" when their velocity exceeds a certain critical value. The fraction of the free ions is equal to $e^{-A/nRT}$, in which $n$ is the number of ions formed from a molecule of the electrolyte. Denoting the Avogadro number by $N$, then the number of free ions is $nNe^{-A/nRT}$. At infinite dilution $A=0$, and the number of free ions $=nN$. From this follows $A=nRT\log_e\mu_\infty/\mu_v$ (1).

Assuming that the marshalling of the ions in solution corresponds with the arrangement of the atoms in the crystallised electrolyte, and that the component ions form a completely saturated electrical doublet, it is possible to calculate $A$ from the charge $E$ carried by the ions and $r$ their distance apart. In the case of a binary electrolyte, the equation is $A=E^2/Dr$, where $D$ is the dielectric constant of the solvent medium and $r=\sqrt[3]{v/2N}$ (2). From equations (1) and (2), the value of $\mu_v$ may be calculated for varying dilutions, and it is shown that the calculated values are in close agreement with those found by experiment between $v=10$ and $v=5000$. The agreement is also good in the case of ternary electrolytes. For bi-bivalent electrolytes, agreement is found for dilutions between $v=10$ and $v=100$, but at $v=1000$ the observed conductivities are much greater than those calculated from the author's formula. The discrepancy is said to be due to hydrolysis.

On account of the diminution of the dielectric constant with rise of temperature, the value of $\mu_v/\mu_\infty$ should decrease. The observed diminution for potassium chloride at 100° is shown to be in satisfactory agreement with that calculated from the author's formula. H. M. D.

**"The Magnetic Properties of Zinc Blende and some other Minerals."** F. STUTZER, W. GROSS and K. BORNEMANN (*Metall und Erz*, 1918, **15**, i, 1—9).—A method is described for measuring the magnetic susceptibility of paramagnetic minerals such as zinc blende, and a list of values of this constant given for fifty-three samples. F. C. T.

**Theoretical and Experimental Investigation of the Thermal Conductivity of Mixtures of Gases.** SOPHUS WEBER (*Ann. Physik*, 1917, [iv], **54**, 481—502).—The theory of the thermal conductivity of gas mixtures is discussed in reference to the experimental data recorded in the literature. New measurements have been made for mixtures of hydrogen and carbon dioxide and of nitrogen and argon, and it is found that the results may be satisfactorily represented by the formula

$$K=K_1/(1+A\,p_2/p_1)+K_2/(1+B\,p_1/p_2),$$

in which $K_1$ and $K_2$ are the thermal conductivities of the constituent gases, $p_1$ and $p_2$ the partial pressures of the components in the mixture for which the conductivity is $K$, and $A$ and $B$ are empirical constants. These constants differ very widely from those which are indicated by theory. In the case of mixtures of hydrogen and carbon dioxide, the values of the constants indicated by theory are $A=1{\cdot}01$ and $B=2{\cdot}56$, whilst the empirical values which satisfy the experimental results are $A=2{\cdot}70$ and $B=0{\cdot}40$. For mixtures of nitrogen and argon, the empirical values are $A=1{\cdot}07$ and $B=0{\cdot}95$. Since the constants are in this case nearly equal, it follows that the thermal conductivity of mixtures is approximately given by the mixture formula, according to which $K=K_1\cdot p_1/(p_1+p_2)+K_2\cdot p_2/(p_1+p_2)$. H. M. D.

**Theory of Specific Heats.** CARL DRUCKER (*Zeitsch. Elektrochem.*, 1918, **24**, 83—84).—Polemical, in which the author criticises the method employed by Jankowsky (this vol., ii, 59) in deducing certain relationships for the specific heat of gases. The deductions drawn from the mathematical expressions are also criticised. J. F. S.

**Specific Heat at Low Temperatures. IV. Measurements of the Specific Heat of Liquid Hydrogen. Preliminary Results on the Specific Heat of Solid Hydrogen and on the Heat of Fusion of Hydrogen.** W. H. Keesom and H. Kamerlingh Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1000—1004. Compare A., 1916, ii, 371).—The apparatus previously described has been used in the determination of the specific heat of liquid hydrogen. According to the most complete of several series of measurements, the atomic heat increases from 1·75 at 14·82° (abs.) to 2·26 at 20·11°.

The data obtained for solid hydrogen gave a mean value of 0·64 at 12·55° for the atomic heat, and for the latent heat of fusion the value 15 was obtained as the mean of two experiments. H. M. D.

**Specific Heats of Lead-Antimony Alloys.** R. Durrer (*Physikal. Zeitsch.*, 1918, **19**, 86—88).—Within the limits of experimental error, the specific heat of alloys of lead and antimony agrees with that calculated from the specific heats of the components by the simple mixture rule. The specific heat (between 0° and 100°) is actually represented by the equation

$$S = 0{\cdot}04965 - 0{\cdot}0001884\,p,$$

where $p$ is the percentage of lead in the alloy. The freezing-point diagram for this pair of metals shows that there are two curves meeting in a eutectic point at 249°. H. M. D.

**Atomic Heats of Tungsten and Carbon at Incandescent Temperatures.** A. G. Worthing (*J. Franklin Inst.*, 1918, **185**, 707—708).—Many of the theories, based on the quantum hypothesis, for explaining the variation of the atomic heat with temperature, lead to the value 5·95 cal. per gram-atom degree as the upper limit for this quantity. With the object of testing these conclusions, the atomic heats of tungsten and carbon have been determined at high temperatures. The elements were used as filaments contained in closed globes at constant pressure; the heating was electrical, and the rate of cooling was determined by means of a potentiometer and a pendulum which operated switches at various points in its path. In the case of tungsten, the atomic heat is shown to vary almost lineally from 6·25 cal. per gram-atom degree at 1200° to 7·35 cal. per gram-atom degree at 2400°. That is, at these temperatures it has an atomic heat which is considerably above the theoretical maximum value, 5·95. In the case of carbon, the value varies from 5·35 at 1200° to 6·05 at 2000°. J. F. S.

**Melting Point Apparatus.** J. C. Hibbert and W. F. Thompson (*Analyst*, 1918, **43**, 216).—A test-tube, 7 inches by 1·4 inches, is supported in a clamp and closed by a cork; the thermometer is attached to a glass tube passing through the cork. The stirrer also passes through a slot in the cork and is supported by rubber rings connected with a bent wire fixed to the clamp stand. The burner is provided with a glass wind-screen. W. P. S.

**Sulphur as a Cryoscopic Solvent.** E. Beckmann and C. Platzmann (*Zeitsch. anorg. Chem.*, 1918, **102**, 201—214).—In spite of the facility with which it undergoes transformation into allotropic modifications, sulphur can be successfully used as a cryoscopic solvent if certain conditions are fulfilled. Soon after having been melted, the freezing point of sulphur is about 119°, but after it has been kept for some hours at a temperature just above its melting point, the freezing point falls to 114·5°, and in this condition the sulphur is suitable for cryoscopic determinations. The apparatus and method employed have been previously described (A., 1897, ii, 88).

The cryoscopic constant of sulphur was determined by means of a number of organic compounds, bromoform (229·3), phenylthiocarbimide (226·6), naphthalene (211·4), diphenyl (208·4), thymol (206·4), quinoline (205·7), β-naphthol (205·2), and aniline (201·8), the mean value of $K$ being 213. The latent heat of fusion $w$, calculated from van't Hoff's equation, is 14·1 gram cal., a value somewhat higher than that determined experimentally for monoclinic sulphur. In accordance with its low dielectric coefficient, 4·0, sulphur shows no dissociating power. Substances of an acidic character like $p$-cresol and α-naphthoic acid show a tendency to associate to double molecules, the value of $K$ falling with increasing concentration.

The "natural" m. p. of sulphur, 114·5°, corresponds with a content of about 3·6% $S_\mu$. The observation of A. Smith (A., 1907, ii, 20), that the attainment of a steady m. p. by sulphur is delayed by sulphur dioxide and accelerated by ammonia, is confirmed. Organic compounds of a neutral or acidic character resemble the former, whilst basic substances, such as pyridine and aniline, resemble ammonia in their behaviour. These substances act catalytically by delaying or accelerating the formation of $S_\mu$, which may itself, however, be formed from $S_\pi$.

Arsenic trisulphide in sulphur has the simple molecule $As_2S_3$, but tends to polymerise with increasing concentration. Selenium tetrachloride shows a molecular weight of half the normal value, and this is attributed to the formation of selenium and sulphur monochlorides. E. H. R.

**Measurement of Low Temperatures. XXVII. Vapour Pressures of Hydrogen in the Neighbourhood of the Boiling Point and between the Boiling Point and the Critical Temperature.** P. G. Cath and H. Kamerlingh Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 991—999. Compare A., 1914, ii, 27).—An improved form of helium gas thermometer is described, and an account is given of the apparatus and methods employed in the further measurement of the vapour pressure of liquid hydrogen at temperatures ranging from the boiling point to the critical point. H. M. D.

**The Saturated Vapour Pressures of Tetratomic Substances.** E. Ariès (*Compt. rend.*, 1918, **166**, 802—805).—On the basis of the vapour pressures of ammonia given in the *Recueil de Constantes physiques*, the formula for the saturated vapour pressures of tetratomic substances is given as $\Pi = \tau^{17/6}Z/x$, where $x=[1+(1-\tau)(0{\cdot}84-\tau)/(\tau^2+1)]\tau^{11/6}$. Whilst the observed values for phosphorus trichloride are in fair agreement with those calculated from this formula, the agreement is not so good in the case of acetylene. W. G.

**The Association of Organic Compounds in Benzene and Alcohol Solution as determined by the Vapour Pressure Method.** William Ross Innes (T., 1918, **113**, 410—435).—The vapour pressures of benzene and ethyl alcohol when mixed with varying quantities of non-volatile substances have been measured at certain fixed temperatures. From the experimental data, the author has calculated the apparent molecular weight of the non-volatile substance by making use of the equation for Raoult's law. If $g$ grams of the substance of molecular weight $m$ are dissolved in $G$ grams of the volatile solvent of molecular weight $M$, and the vapour pressures of the pure solvent and solution are $p$ and $p'$, then this equation may be written in the form $m'=gMp'/G(p-p')$, where $m'$ is the apparent molecular weight of the non-volatile solute. The results obtained are shown by means of curves, in which $m'/m$ is plotted as a function of the percentage molecular concentration of the solute.

When benzene is used as solvent, the curves obtained may be divided into groups. In one of these, the substances have values of $m'/m$ which differ but little from unity even when the molecular concentration of the substance is very large. Acids and oximes form a group showing considerable association. In the case of formanilide and acetanilide, the value of $m'/m$ increases rapidly with the concentration, and a maximum appears to be reached. Ethyl tartrate is extremely abnormal in that very high values are found for $m'/m$, which reaches a maximum when the percentage molecular concentration is about 50 and diminishes rapidly at higher concentrations.

In alcohol as solvent, four substances were examined, and all gave values of $m'/m$ which increase with the concentration. In the case of azobenzene, which is readily soluble in hot alcohol, the association factor seems to increase continuously with the concentration. The value of $m'/m$ obtained for this substance in 60% solution is about 6·0.

The theoretical interpretation of the results is discussed in some detail, and in this connexion attention is directed to results obtained for mixtures of sulphuric acid and water (compare T., 1904, **85**, 1345), according to which the apparent molecular weight is very small and decreases rapidly with increasing concentration.

H. M. D.

**Heats of Dilution and their Variations with Temperature.** FRANK R. PRATT (*J. Franklin Inst.*, 1918, **185**, 663—695).—The heat of dilution of solutions of a large number of salts has been determined at a series of temperatures with the object of testing the validity of the expression $dl/d\theta = -dH/dm$, in which $l$ is the heat of dilution, $\theta$ the temperature, $m$ the mass of the solution, and $H$ the heat capacity of the system. The measurements were made by the method of constant flow, in which two streams, of solution and water respectively at the same temperature, were allowed to mix continuously in a Dewar vessel at constant temperature. Solutions of sodium chloride, potassium chloride, barium chloride, strontium chloride, ammonium chloride, sodium hydroxide, potassium hydroxide, sodium nitrate, potassium nitrate, barium nitrate, strontium nitrate, and ammonium nitrate were used. The results indicate that in a general way the above formula is true. The discrepancies are discussed. A further series of measurements was made with the following non-electrolytes: resorcinol, dextrose, sucrose, catechol, quinol, mannose, and ethyl alcohol. The chief point of interest arising from these experiments is that for non-electrolytes $H$ is constant for all concentrations; on the whole, the results here are in general agreement with the above formula.

J. F. S.

**Possibility of Calculating the Properties of Liquids and Vapours.** JOHANNES GEISSLER (*Zeitsch. Elektrochem.*, 1918, **24**, 101—113).—A theoretical paper in which the author has shown that for the four substances fluorobenzene, benzene, ethyl ether, and carbon tetrachloride there is a region in which the physical properties can be represented by straight lines, and that within the limits of this area the physical properties can be calculated. Methods are worked out for calculating (1) the molecular volume of the saturated vapour from that of the liquid, (2) the molecular volume of a liquid from the temperature, (3) the coefficient of expansion of a liquid from the temperature, (4) the vapour pressure of a liquid from the temperature, (5) the change of vapour pressure per degree at a given temperature, (6) the latent heat of vaporisation of a liquid at a given temperature. The calculated and experimental values are compared, and it is shown that whilst there is good agreement in many cases, there are also divergences. The latter are attributed to the use of data obtained in a region removed from the limited region mentioned above, or from data in the neighbourhood of the freezing point.

J. F. S.

**Atomic and Molecular Numbers.** HERBERT STANLEY ALLEN (T., 1918, **113**, 389—396).—A short account is given of the significance of the atomic number in connexion with the periodic classification of the elements. The atomic numbers of analogous elements differ by eight or a multiple of eight, or in some cases by a number which is two units greater than one of the foregoing. The reason for these variations from the rule of eight is the presence of three elements in group VIII of the periodic table.

Molecular numbers of analogous compounds show similar relations. In reference to organic compounds, it is pointed out that the molecular number for the group $\cdot CH_2\cdot$ is eight, and the rule of eight is consequently of wide application in organic chemistry. It is probable that many properties of chemical compounds will be found to depend on the values of the molecular numbers.

H. M. D.

**Modified Mercurial Viscosimeter for Determining the Viscosity of Volatile Liquids.** F. M. Lidstone (*J. Soc. Chem. Ind.*, 1918, **37**, 148—149T).—In the apparatus described, an attachment is provided by means of which an equal excess pressure may be applied above and below the moving column of liquid in the viscometer. This prevents the formation of a cushion of vapour between the mercury and the volatile liquid under examination, but does not interfere with the usual constants of the instrument.

W. P S.

**The Viscosity of Liquefied Gases. X. The Viscosity of Liquid Hydrogen.** J. E. Verschaffelt (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 986—990. Compare A., 1917, ii, 408).—From observations on the time of oscillation of a specially designed oscillatory system immersed in the liquid hydrogen, the viscosity at 20·4° (abs.) has been found to be $\eta=0{\cdot}000130$, with an estimated accuracy of about 1%. A preliminary determination of the viscosity of the saturated vapour at this temperature (vapour pressure = 76·9 cm.) gave $\eta=0{\cdot}000010$.

H. M. D.

**Solubility Measurements.** Stewart J. Lloyd (*J. Physical Chem.*, 1918, **22**, 300—302).—The measurements recorded were made incidentally in connexion with other work. The solubility of sulphur dioxide in benzene, toluene, nitrobenzene, *o*-nitrotoluene, and acetic anhydride was measured at various temperatures. At 20°, the solutions saturated at 756—760 mm. contain the following amounts in grams per litre: toluene, 236·0; nitrobenzene, 267·4; *o*-nitrotoluene, 236·0; acetic anhydride, 106. The solubility of aluminium chloride in carbon tetrachloride decreases from 0·74 at 4° to 0·06 gram per litre at 34°; in chloroform, from 1·00 at 0° to 0·72 at 25° and 0·65 at −15°. The solubility of barium chloride in nitrobenzene increases from 0·167 at 20° to 0·40 at 100°, and that of benzoic acid in ethyl acetate from 8·0 grams per litre at −6·5° to 37·7 at 21·5° and 95·7 at 75°.

H. M. D.

**Reactions between Solid Substances.** Leslie Henry Parker (T., 1918, **113**, 396—409. Compare T., 1914, **105**, 1504).—The rate at which certain solid substances react together has been examined systematically by observations at various temperatures up to and above the fusion temperature. The pairs of substances investigated were sodium carbonate and barium sulphate, silver nitrate and sodium carbonate, cuprous chloride and sodium carbonate. In all cases, the mixtures were made from carefully dried substances. Although the results obtained show clearly that reaction takes place below the fusion temperature, and that the rate of the reaction between the solids increases continuously with rise of temperature, there is in all cases a very marked increase in the velocity at the temperature of fusion. The ratio of the velocity in the fused mixture to that at the highest temperature in the solid state varies in the three cases examined. It is immeasurably large in the mixture containing barium sulphate, is equal to about 150 for the mixture containing silver nitrate, and to about 20 for the mixture containing cuprous chloride.

The results seem to show that the liquid state *per se* has an influence on the rate of interaction, which influence is to be distinguished from that of temperature. The fact that shearing stresses give rise to reactions between solid substances does not seem as yet to be completely explained, and it is suggested that such stresses produce changes of state in the surface layers which are equivalent to that produced by fusion. H. M. D.

**Xanthic Acids and the Kinetics of their Decomposition. I.** Hans von Halban and Walter Hecht (*Zeitsch. Elektrochem.*, 1918, **24**, 65—82. Compare A., 1913, ii, 312).—The rate of decomposition of xanthic acid [ethyl hydrogen dithiocarbonate, OEt·CS·SH] and methyl hydrogen dithiocarbonate in water at 0° has been studied. The solubility of these substances in water was first determined, and found to be at 0°: xanthic acid, 0·02 mol. per litre; methyl hydrogen dithiocarbonate, 0·05 mol. per litre. The rate of decomposition was determined by dissolving a known amount of the sodium salt of the acid in question in water, and, when the solution had reached 0°, liberating the acid with a slight excess of hydrochloric acid, then after a measured interval of time neutralising with a cooled solution of sodium hydrogen carbonate and titrating with a 0·02*N*-iodine solution. It is shown that, contrary to the behaviour of solutions in organic solvents, the velocity constants in the present case, when calculated on the basis of a unimolecular reaction, decrease rapidly with decreasing concentration; the decomposition is positively catalysed by hydrogen ions. This leads to the assumption that both the undissociated molecules and the ions take part in the reaction. On the basis of this assumption, the dissociation constants of the acids were calculated, and found to be independent of the dilution, a fact which confirms the assumption. At 0°, the dissociation constant for methyl hydrogen dithiocarbonate is found to be 0·034, and that for xanthic acid 0·030. The addition of sulphates (Na, Mg, $NH_4$) to the decomposing xanthic acids in water solution strongly retards the action; for example, 0·25*N*-magnesium sulphate reduces the velocity of decomposition to one-third of the original value, and 3*N*-ammonium sulphate reduces it to one-sixth. A few velocity measurements have been made in ethyl alcohol, methyl alcohol, propyl alcohol, amyl alcohol, and benzyl alcohol solutions to complete the data published in an earlier paper (*loc. cit.*). Measurements were made at 0° on the partition of xanthic acid between water and carbon disulphide, chloroform, nitrobenzene, light petroleum, benzyl alcohol, and amyl alcohol respectively. It is shown that the dependence of the partition coefficient on the dilution is in accord with the dissociation constant calculated from the velocity values. The absorption spectrum of solutions of xanthic acid in light petroleum, 0·5*N*-ethyl alcohol in light petroleum, and in diethyl ether was measured, but although the rate of decomposition is very different in the different solvents, no difference could be observed in the absorption curves. Benzyl hydrogen dithiocarbonate was prepared from the potassium salt. This substance is a solid, m. p. 29°, and when quite pure may be kept for several hours, and in non-hydroxy-solvents has a normal molecular weight. The solubility and rate of decomposition have been determined in twelve solvents. The saturated solution at 0° has the following concentration in these solvents: hexane 0·224*N*, light petroleum 0·316*N*, methyl alcohol 0·36*N*, acetic acid 0·41*N*, nitromethane 1·49*N*, acetonitrile 3·26*N*, carbon disulphide 3·70*N*, acetone 3·41*N*, diethyl ether 2·93*N*, benzene 3·33*N*, ethyl bromide 3·88*N*, and nitrobenzene 3·15*N*. The van't Hoff velocity constant was calculated from the data, and these values, as well as those for xanthic acid, show that the catalytic influence of the solvent is not removed by the van't Hoff calculation. J. F. S.

**Hydrolysis of Ethyl Citrate and the Ethyl Hydrogen Citrates.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1918, **24**, 84—85).—Polemical; the author claims that the work of Pinnow (this vol., ii, 103) is not the first case in which the hydrolysis of a tribasic ester has been studied, and then proceeds to criticise the results published by Pinnow. J. F. S.

**The Influence of Lipoids on the Rate of Reaction.** M. SIEGFRIED (*Biochem. Zeitsch.*, 1918, **86**, 98—109).—Lecithin inhibits the transformation of the yellow mercuric iodide into the red variety, and also the reduction of ammoniacal silver nitrate by phenylhydrazine. The latter reaction should be carried out in the dark, and in the presence even of diffuse sunlight the inhibiting action of the lipoid is diminished. S. B. S.

**Ester Catalysis of γ-Lactones.** HJALMAR JOHANSSON and HUGO SEBELIUS (*Ber.*, 1918, **51**, 480—485).—It has recently been shown that the hydrolysis of β-lactones to the hydroxy-acids is not catalysed by hydrogen ions (*Lunds universitets årsskrift*, 1916), and it appeared to be of interest, therefore, to determine directly whether the hydrolysis of γ-lactones, like the formation of them (compare Taylor and Close, A., 1917, ii, 253), is catalysed by acids.

For this purpose, the catalysis of the hydrolysis of γ-valerolactone and γ-butyrolactone by nitric acid has been studied, the hydroxy-acid being titrated by means of barium hydroxide. It is found that in the case of γ-butyrolactone, with quantities of nitric acid represented by 9, 3, and 1, the time required for the production of the same percentage of hydroxy-acid is represented very nearly by 1, 3, and 9. The results with valerolactone are similar; H-ion concentration, 6:3:1 (roughly), and times, 1:3:6. The hydrolysis of γ-lactones is therefore a normal case of ester catalysis.

J. C. W.

**Errors affecting Determinations of Atomic Weight. VII. Refinements in the Method of Weighing: Microbalance: Application to the Atomic Weight of Helium and Hydrogen.** PH. A. GUYE (*J. Chim. Phys.*, 1918, **16**, 46—61. Compare A., 1916, ii, 385, 386, 432, 435; this vol., ii, 40, 41).—The Taylor microbalance is discussed by the author and shown to be very suitable for the accurate determination of gaseous densities. Correct formulæ are developed for calculation of the density and molecular weight of gases from the experimental figures obtained in this way. These formulæ have been applied to the experimental figures obtained by Taylor (*Phys. Review*, 1917, **10**, 653), when the following values were obtained: normal litre of hydrogen weighs 0·089858 gram, molecular weight 2·0151; normal litre of helium weighs 0·17835 gram, molecular weight 3·9976. These values differ by about 10 per 10,000 from those calculated by Taylor. It is further shown that the Taylor microbalance appears to be susceptible of a few improvements, which are indicated by the author, and which, being made, give an instrument which will not only give the densities and molecular weights of gases with a precision at least equal to that of other methods, but which, with very small quantities of material, will give all the weighings necessary for the determination of atomic ratios. The great interest of the method lies in the fact that the determination of mass will resolve itself into the measurement of length, which is much more precise than weighing with weights, no matter how carefully calibrated.

J. F. S.

**The Conception of the Chemical Element and the Phenomenon of Isotopy (Addendum).** K. FAJANS (*Jahr. Radioaktiv. Elektronik*, 1918, **15**, 101—102. Compare A., 1917, ii, 566).—In further pressing the point of view that isotopic elements cannot be considered as one element, in Boyle's sense of undecomposability, an intimate mechanical mixture of isotopes is postulated as capable of being made and of existing as such in nature, which, since they can be imagined to be capable of being resolved into their constituents, if of different density, by the use of suitable fluids, cannot be regarded as undecomposable.

F. S.

**Molecular Frequency and Molecular Number. III. Inorganic Compounds. Lindemann's Formula.** H. STANLEY ALLEN (*Phil. Mag.*, 1918, [vi], **35**, 445—460. Compare this vol., ii, 163).—According to Lindemann, the characteristic molecular frequency of a compound is given by the formula $\nu = k\sqrt{T_s/MV^{\frac{2}{3}}}$, in which $M$ is the molecular weight, $V$ the molecular volume, and $T_s$ the melting point of the compound on the absolute scale. Assuming $k = 3{\cdot}08 \times 10^{12}$, this formula has been used to calculate the frequency for a large number of inorganic compounds. The results, which are arranged according to the periodic groups, afford further evidence of the validity of the relation $N\nu = n\nu_A$ or $N\nu = (n + \frac{1}{2})\nu_A$, according to which the product of the molecular number and the characteristic frequency is a simple multiple of the fundamental frequency $\nu_A$.

The fact that this relation holds for compounds which include elements belonging to all the different groups of the periodic system makes it appear very probable that the above equation is the expression of a relation which is of fundamental importance and characteristic of the solid state of matter. H. M. D.

**Periodic System of the Elements.** CHARLES P. STEINMETZ (*J. Amer. Chem. Soc.*, 1918, **40**, 733—739).—It is shown that the single, double, and quadruple periodicities which characterise the periodic system can be completely represented by a Riemann surface having two singular points at $-40$ and $-130$. Incidentally, it is pointed out that it is unjustifiable to assume that the functional relation between the properties of the elements and their atomic weights can be represented on a plane. H. M. D.

**The Ductility of Metals and their Position in the Periodic System.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 247—254; from *Chem. Zentr.*, 1918, i, 509—510).—Lothar Meyer indicated that the ductile elements lie near the maxima and minima of the atomic volume curve. The author regards the occurrence of ductility as dependent on the formation of as many slip-planes as possible in the direction of main extension and the occurrence of movement with as little force as possible, and he uses the term ductility in the commonly accepted sense of capacity to be drawn into wire. Pairs of elements which form a continuous series of mixed crystals are regarded as isomorphous, so that by starting from a known crystal lattice it is possible to find many other examples of the same type. In the periodic system, a certain symmetry prevails in the crystalline form of the typical crystals, but is interrupted by the non-metallic elements of the carbon group. Elements with various crystalline forms are ductile. The ductility is not dependent on any definite space lattice, but probably on the occurrence of only one kind of atoms, between which no valencies are active, in the lattice of their crystals. If the valencies between the atoms of the lattice become active, as in the binary compounds of the metals, the formation of slip-bands is checked and the ductility disappears. D. F. T.

**The Relationship of the Rare Earths to the Periodic System.** Rudolf Vogel (*Zeitsch. anorg. Chem.*, 1918, **102**, 177—200).—The many attempts which have been made to fit the elements of the rare earths into existing groups of the periodic classification have all been unsatisfactory. There is only slight chemical and crystallographic justification for placing lanthanum in the third and cerium in the fourth group, and in any case the valency of an element or the isomorphism displayed by certain of its salts serves as a very uncertain guide to its true relationship to other elements. The author agrees with Tammann that an element should show little or no chemical affinity for another element belonging to the same group; conversely, if two elements form a stable compound, they cannot belong to the same group. When this test is applied to the only rare earth element which is available in sufficient quantity for systematic study, cerium, it must be concluded that this element can belong to none of the ordinary groups of the periodic system. It forms binary compounds with metals of every group, with the exception of those of groups VI and VII, which have not been studied, and many of these compounds are remarkable for their great heats of formation and high melting points. In particular, cerium combines energetically with elements of groups III, IV, and V to form such compounds as $CeAl_2$ (m. p. 1460°), $CeAl_4$ (m. p. 1250°), $Ce_2Sn$ (m. p. 1400°), and $Ce_4Bi_3$ (m. p. 1630°), whilst lanthanum also forms with aluminium a strongly exothermic compound, $LaAl_4$, of high melting point.

The new periodic law, based on the atomic numbers of the elements, requires the existence of sixteen elements between Ba(56) and Ta(73). Of these, fourteen rare earth elements are known, one being missing between Nd and Sm, and one between Lu and Ta. Whilst, therefore, the sixteen rare earth elements must form a continuous series with the remaining elements, they must form a special group by themselves.

A satisfactory representation of the position of the rare earth group in the family of elements is obtained in the following manner. The elements are arranged in order of atomic numbers on an ascending spiral, each turn of which corresponds with one short period of eight elements, elements belonging to the same group appearing vertically above one another. After passing Ba, the spiral changes its course and develops a subsidiary, smaller loop which, after making rather more than a complete turn, rejoins the original path of the spiral at Ta, group V. On this subsidiary loop are crowded the sixteen rare earth elements, which form a closely related family independent of the other groups situated on the main spiral. The elements La and Ce appear on the small loop in fairly close proximity to the vertical lines through groups III and IV respectively on the principal spiral, and this may account for certain properties shown by La and Ce in common with the elements of groups III and IV respectively. The rare earth elements themselves exhibit a certain periodicity in their basicity, magnetic properties, and in the solubility of their salts;

such periodicity or gradual change of properties is to be inferred from the form of the loop.

It is further suggested that the triads Fe,Co,Ni, Ru,Rh,Pd, Os,Ir,Pt also form three secondary loops on the principal spiral in place of elements belonging to group VIII. Each triad then forms a sub-group similar in character to the rare earth group, and homologous elements of the three triads appear on vertical lines parallel to the axis of the spiral. It is significant that the typical magnetic elements Fe, Co, Ni, and also the strongly paramagnetic elements Tb, Dy, and Ho, are all among those elements which do not conform to the normal course of the periodic system. E. H. R.

**Gas Generating Apparatus.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 64).—An apparatus for generating small quantities of hydrogen sulphide, carbon dioxide, hydrogen, etc., consists of a wide tube constricted at its middle so as to form two short, cylindrical bulbs; the upper bulb is provided with a tap and contains the ferrous sulphide or calcium carbonate, etc., whilst the lower bulb is connected by a glass tube to an acid reservoir at some height above the bulbs. The whole apparatus is made in one piece. W. P. S.

**Experimental Retort for Dry Distillation.** F. E. COOMBS (*Met. and Chem. Eng.*, 1918, **18**, 425).—The retort consists of a cylinder of metal closed at the bottom. A similar cylinder, but of slightly larger diameter, so as to slide loosely over the retort, forms the lid, to which a bent delivery tube is fitted. The lid is secured to the retort by screws. The apparatus is placed in a bath of fused metal or sodium hydroxide, the level of which is below the top of the retort, which is now sealed by the liquid entering the annular space inside the lid. The contents of the retort can be distilled at a known and regulated temperature. The advantage claimed is accessibility for cleaning and charging. H. J. H.

**Extraction Apparatus for the Laboratory.** CARL G. SCHWALBE and WALTER SCHULZ (*Chem. Zeit.*, 1918, **42**, 194).—A modification of the Besson extractor (A., 1916, ii, 26) in which no corks are employed and larger quantities (4—6 litres) of material may be extracted. The apparatus consists of a white metal cylinder in the upper part of which is fitted a wire ring which carries a fine cotton bag holding the material to be extracted. Above this bag is fitted a cylindrical condenser, through which a stream of water flows. The apparatus stands in a water-bath heated by a gas burner in the usual manner. All gas- and water-connexions are made of metal so as to ensure the safety of the apparatus. A. B. S.

**Simple Arrangement for Simultaneous Stirring and Filtration.** FRITZ FEIGL (*Zeitsch. angew. Chem.*, 1918, **31**, i, 68).—To obviate the errors which occur when portions of a saturated solution at high temperatures are removed for solubility determinations, the author describes a combined stirrer and filter. The apparatus consists of a stout-walled, wide test-tube from which the bottom has been removed, and on to the sides of which a number of glass vanes have been fastened. One end of the tube is covered with a piece of linen or hardened filter paper, the other end is inserted into a hole in a wooden pulley. The tube is then partly immersed in the saturated solution and rotated; the clear, saturated solution slowly filters into the tube, whence it can be withdrawn in suitable quantities. If a semipermeable membrane is substituted for the filter paper, the apparatus may be used to determine the velocity of diffusion of colloids below their coagulation temperature.

J. F. S.

**Grinding Glass Tips for Drop-weight Apparatus.** EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1918, **40**, 784—785).—For the measurement of surface tension by the drop weight method, it is necessary to prepare capillary tips of circular cross-section by grinding until the section is flat and smooth and the edges are perfectly sharp. To facilitate this, the author recommends the use of Wood's metal or other similar low melting alloy. The glass tube, made ready for the final adjustment of the tip, is lowered into the molten alloy, some of which is drawn into the capillary. The tube is left in position until the alloy has solidified, when the tip becomes firmly embedded in the alloy. The tube and alloy are then ground until the requisite sharp edge is obtained.

H. M. D.

**Willem Homberg.** F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 602—605).—Further particulars of the life of the alchemist Homberg, including a reproduction of part of an autograph letter (compare this vol., A., ii, 164).

A. J. W.

**Anselmus Boëtius de Boodt.** F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 628—671).—An account of the life and researches of the mineralogist de Boodt, who was born at Bruges in 1550, and died at the same place on June 21st, 1632.

A. J. W.

**Lecture Experiments for Demonstrating the Law of Multiple Proportions.** F. EMICH (*Zeitsch. anal. Chem.*, 1918, **57**, 65—71).—Simple experiments are described, and comprise the estimation of oxygen in cupric and cuprous oxides by reduction with hydrogen, the formation of normal potassium tartrate and potassium hydrogen tartrate, and the gasometric estimation of carbon dioxide in sodium carbonate and sodium hydrogen carbonate.

W. P. S.

**Some Lecture Experiments with Silver Carbide. [Acetylide].** JOHN EGGERT and HANS SCHIMANK (*Ber.*, 1918, **51**, 454—456. Compare A., 1917, ii, 462).—The experiments are designed to show that pure silver carbide detonates very mildly in a vacuum, its bursting power under ordinary conditions being due to the rapid heating and expansion of the surrounding air.

J. C. W.

# Inorganic Chemistry.

**The Relation of Iodine to Sulphur and Selenium.** E. BECKMANN and C. PLATZMANN (*Zeitsch. anorg. Chem.*, 1918, **102**, 215—222).—The molecular weight of iodine determined cryoscopically in sulphur (K = 213) corresponds with $I_2$. Sulphur dissolved in iodine has the molecular composition $S_8$, but in the same solvent, selenium is dissociated into $Se_2$ and $Se_1$, although in organic solvents it exists as $Se_8$, and iodine, on account of its low dielectric constant, would not be expected to have dissociating properties. The freezing point of sulphur is raised by selenium, as is to be expected, since the two substances are isomorphous. On account of the sparing solubility of selenium in sulphur, experimental determinations were limited to concentrations up to 2·5% Se. Over this range, the elevation of the freezing point was approximately proportional to the concentration, and averaged 0·242° per 1% Se. It is concluded that in sulphur–selenium mixtures the latter is present as $Se_8$.

The depression of the freezing point of sulphur–selenium mixtures by iodine and diphenyl was determined. The cryoscopic constants of mixtures containing up to 1·58% Se were found to be practically equal to that of sulphur alone. On the assumption that the change of the freezing point of sulphur containing selenium and iodine is the algebraic sum of the elevation due to $Se_8$ and the depression due to $I_2$, the total effect was calculated and the result compared with the observed value for a number of concentrations. The agreement was generally satisfactory. There is no evidence of the formation of a compound between selenium and iodine, and the low molecular weight of selenium in iodine solution remains unexplained. E. H. R.

**Action of Thionyl and Sulphuryl Chlorides on Sulphur and Phosphorus.** H. B. NORTH and J. CLAUDE THOMSON (*J. Amer. Chem. Soc.*, 1918, **40**, 774—777).—Thionyl and sulphuryl chlorides were heated in sealed glass tubes with sulphur and phosphorus at temperatures ranging from 70° to 180°. Both chlorides react with sulphur at 150° to 180°, with the formation of sulphur dioxide and sulphur monochloride. Under similar conditions, the two chlorides react with both red and yellow phosphorus, with the formation of phosphorus trichloride, according to the equations $3SO_2Cl_2 + 2P = 2PCl_3 + 3SO_2$, $4SOCl_2 + 2P = 2PCl_3 + 2SO_2 + S_2Cl_2$. Prolonged heating tends to produce phosphorus pentachloride in accordance with the equations $PCl_3 + SO_2Cl_2 = PCl_5 + SO_2$, $3PCl_3 + 4SOCl_2 = 3PCl_5 + 2SO_2 + S_2Cl_2$, but these reactions are far from complete after heating for several hours at 160—180° in presence of considerable excess of the sulphuryl or thionyl chloride. H. M. D.

**Oxidation of Sulphur Dioxide and Ammonia in the Presence of Platinum and Rhodium.** P. Wenger and C. Urfer (*Ann. Chim. anal.*, 1918, **23**, 97—104).—Maximum oxidation of sulphur dioxide takes place at 432° in the presence of platinum black, 96·8% of the dioxide being converted into sulphur trioxide. When rhodium black is used as the catalyst, the maximum oxidation (91·1%) occurs at 610°. In the case of ammonia, 97% is converted into nitric and nitrous acids by platinum black at 533° to 562°, whilst with rhodium black a maximum oxidation of 69·7% is attained at 662°. W. P. S.

**Synthesis of Ammonia at High Temperatures. II.** Edward Bradford Maxted (T., 1918, **113**, 386—389. Compare *ibid.*, 168).—Further observations on the combination of nitrogen and hydrogen at high temperatures have been made by passing the 1 : 3 mixture through a capillary tube fitted with platinum wire electrodes, between which sparks were made to pass by connecting the wires with an induction coil. When the distance between the electrodes is gradually reduced, the ordinary spark discharge is transformed into a small high-tension arc characterised by a continuous flame of high temperature. In experiments in which the rate of passage of the gas was kept constant and the size of the gap reduced, it was found that this was accompanied by a continuous increase in the percentage of ammonia formed. Similar results were obtained when the speed of the gas was controlled so as to give a constant time of contact. For a fixed width of gap, the percentage of ammonia was found to increase as the rate of flow of the gaseous mixture diminished. The results generally are in agreement with those obtained in the previous high-temperature measurements (*loc. cit.*). H. M. D.

**Synthesis of Nitrosyl Bromide.** E. Moles (*J. Chim. Phys.*, 1918, **16**, 3—10; *Anal. Fis. Quim.*, 1918, **16**, 377—385).—The author has examined the reaction of nitric oxide on bromine, and the nature of the resulting nitrosyl bromide, with the object of ascertaining whether this substance is suitable for use in the determination of the atomic weight of bromine by the method employed by Wourtzel (A., 1913, ii, 771) for chlorine with nitrosyl chloride. After a series of very careful experiments, it is found that the nitrosyl bromide produced always contains a slight excess of bromine, and consequently the compound is of no use for the purpose of determining atomic weights. J. F. S.

**Preparation of Carbon Tetrachloride from Carbon Disulphide and Chlorine.** Isco Chemical Co. (U.S. Pats. 1260621 and 1260622).—Carbon disulphide containing free sulphur is treated with chlorine in the presence of a catalyst to form sulphur dichloride and carbon tetrachloride, and an additional quantity of carbon disulphide is then added to convert the sulphur dichloride into sulphur monochloride, with the formation of more carbon tetrachloride. The product is treated with sufficient tin to convert the sulphur monochloride into sulphur, with the formation of stannic chloride, and, after separating the sulphur, water is added to hydrate the stannic chloride, and the carbon tetrachloride is recovered from the mixture by distillation. A. S.

**Causticising of Potassium Carbonate.** E. BELLONI (*Ann. Chim. Applicata*, 1918, **9**, 115—149).—The reaction between potassium carbonate and calcium hydroxide is reversible, and may be represented as a heterogeneous system in which there are two solid phases and one liquid phase containing variable proportions of the other components. From mathematical data based on the consideration of the formulæ of Bodländer and Lucas (A., 1905, ii, 634) and Le Blanc and Novotny (A., 1907, ii, 22), the following general isotherm for the conversion of an alkali carbonate into hydroxide by the action of calcium hydroxide has been deduced: $C^2{}_{\mathrm{KOH(NaOH)}}C/{}_{\mathrm{K_2CO_3(Na_2CO_3)}} = a - a'\phi + a''\phi^2$, where $C^2{}_{\mathrm{KOH}}$ represents the concentration in gram-molecules of alkali hydroxide, $C_{\mathrm{K_2CO_3}}$ the concentration of the alkali carbonate in the final solution, and $\phi$ the concentration of the carbonate in the initial solution. The constant $K$, which represents any given concentration giving stable equilibrium, is a definite function of $\phi$ to which the form may be given $K = a - a'\phi + a''\phi^2$. In the special case of the conversion of potassium carbonate into hydroxide at 100°, and for values of $\phi$ varying from 0 to 1·5 (that is, for solutions up to $3N$), the equation assumes the form $C^2{}_{\mathrm{KOH}} / C_{\mathrm{K_2CO_3}} = 133{\cdot}20 - 127{\cdot}85\phi + 43{\cdot}50\phi^2$. The yield of potassium hydroxide obtainable from a solution of potassium carbonate of known concentration may be calculated by means of the equation $C_{\mathrm{KOH}} = K(-0{\cdot}25 + \sqrt{0{\cdot}0625 + \phi/K})$. At equal molecular concentration of the solutions and under the same conditions of temperature, a greater yield of hydroxide is obtained from sodium carbonate than from potassium carbonate. The formation of a double carbonate of potassium and calcium at a given temperature is only possible at a single definite concentration, which at 100°, the temperature for technical preparation of hydroxide, is 61·78 grams per 100 c.c. This corresponds with a concentration much higher than is used in the manufacturing process. The temperature has a great influence on the velocity of the reaction, but does not affect the final stage of equilibrium. The results for equal concentrations, $\phi$, at 80° and 100° were practically identical. [See also *J. Soc. Chem. Ind.*, 368A.] C. A. M.

**Equilibria in Solutions containing Mixtures of Salts. I. The System Water and the Sulphates and Chlorides of Sodium and Potassium.** W. C. BLASDALE (*J. Ind. Eng. Chem.*, 1918, **10**, 344—347).—The conditions which govern the separation by fractional crystallisation of sodium and potassium salts were investigated by the aid of the phase rule diagrams for such solutions. The equilibrium conditions of the reversible reaction $3KCl + 2Na_2SO_4,10H_2O \rightleftharpoons K_3Na(SO_4)_2 + 3NaCl + 20H_2O$ were studied, and the compositions of the solutions saturated with one or more of these salts at 0°, 25°, 50°, 75°, and 100° were determined and plotted with respect to four axes representing sodium sulphate, potassium sulphate, potassium chloride, and sodium chloride. The diagrams represent the composition of all possible solutions which can be in equilibrium with these four salts, and with Glauber's salt and sodium potassium sulphate (glaserite), and indicate the stability of glaserite under widely varying conditions. [For details, see *J. Soc. Chem. Ind.*, 369A.]

W. F. F.

**Separation of Sodium and Potassium Chlorides and Sulphates by Fractional Crystallisation.** W. C. Blasdale (*J. Ind. Eng. Chem.*, 1918, **10**, 347—353).—The application of the principles described in the preceding abstract to the separation of mixed solutions is shown. Diagrams are given representing the composition of mixed solutions of (1) potassium chloride and sodium chloride, (2) potassium chloride and potassium sulphate, (3) potassium sulphate and sodium sulphate, (4) sodium sulphate and sodium chloride, and (5) mixtures of potassium salts with sulphates and chlorides of sodium and potassium. The diagrams are used to determine possible cycles of operation by which the various salts may be successively crystallised by evaporating and cooling at suitable temperatures. [For details, see *J. Soc. Chem. Ind.*, 369A.]

W. F. F.

**Production of a Stable Sodium Percarbonate.** Henkel & Co. (D.R.-P., 303556, 1915; from *Chem. Zentr.*, 1918, i, 497).—A compound, $2Na_2CO_3,3H_2O_2$, is obtained by the addition of sodium carbonate to an aqueous solution containing at least a sesquimolecular proportion of hydrogen peroxide; instead of sodium carbonate and hydrogen peroxide being taken as such, these substances may be produced in the solution by a suitable chemical change, for example, from sodium peroxide and sodium hydrogen carbonate.

D. F. T.

**The Calcium Arsenates.** R. H. Robinson (*J. Agric. Res.*, 1918, **13**, 281—294).—Pure calcium hydrogen arsenate was prepared by pouring a calcium chloride solution slightly acidified with acetic, hydrochloric, or nitric acid into a sodium hydrogen arsenate solution similarly acidified. A heavy, voluminous precipitate was formed, which was washed by decantation, filtered, washed with hot water until free from chlorides, and dried at 100°. The washings were evaporated to a small volume, when crystals separated, and were washed and dried. Analysis showed both the powder and crystals to have the formula $CaHAsO_4,H_2O$. The water of crystallisation was lost at 175°.

Pure tricalcium arsenate was prepared by pouring an alkaline calcium chloride solution into an alkaline sodium hydrogen arsenate solution. A heavy, voluminous precipitate was formed, which was washed by centrifuging and decantation, and then filtered and dried at 100°. Analysis agreed with the formula $Ca_3(AsO_4)_2,2H_2O$. The water of crystallisation was lost at 175°.

The specific gravity of the salts was determined by weighing in specially dehydrated absolute alcohol at 20°. The results were: for $CaHAsO_4,H_2O$, $D_4^{20}$ 3·09; for $CaHAsO_4$, 3·48; for $Ca_3(AsO_4)_2,2H_2O$, 3·23; for $Ca_3(AsO_4)_2$, 3·31. Solubility was determined at 25° in a water-bath fitted with a revolving bottle-holder. One hundred grams of the solution contained in the case of $CaHAsO_4$ 0·3108 gram of the salt, and in the case of $Ca_3(AsO_4)_2$ 0·0133 gram.

J. H. J.

**An Artificial Patina.** OTTO GROTIAN (*Zeitsch. Elektrochem.*, 1918, **24**, 83).—The author describes a method of artificially producing an incrustation or patina on copper articles similar to that found on ancient bronzes. This film is produced by electrolysing a solution of copper sulphate between copper electrodes for three minutes with a current density of 1 amp./per sq. decimetre; the current is then interrupted and the cathode removed from the liquid. The anode is allowed to remain undisturbed in the liquid for twenty-four hours. The process is repeated several times, alternately passing the current for three minutes and leaving the anode for twenty-four hours. After several repetitions, the anode is removed and found to be covered with a beautiful bluish-green, non-crystalline patina, which cannot be removed by washing. On analysis, the film is shown to have the composition $CuO,3H_2O$.

J. F. S.

**Mercury Fulminate and its Estimation.** G. S. HEAVEN (*J. Soc. Chem. Ind.*, 1918, **37**, 143—147T).—Commercial mercury fulminate consists of a crystalline powder varying in colour from pale cream to dark brown; the largest crystals do not exceed 1 mm. in length, and these are more sensitive to impact than are the smaller crystals. A very fine powder, sifted through calico, fails to fire. Fulminate is soluble in alcohol, ammonia, pyridine, potassium cyanide solution, and in cold water, but is decomposed by hot water, alkali solutions, and thiosulphate solution. It does not inhibit the growth of fungi; *Tricoderma viride* and *Acrostalagmus albus Preuss* grow readily on bags containing fulminate, and even on the crystals themselves. The following method is recommended for the analysis of detonator composition containing fulminate, antimony sulphide, potassium chlorate, etc. A quantity of 0·3 gram of the sample is treated with 50 c.c. of *N*/10-thiosulphate solution, 0·3 gram of boric acid is added, the mixture is stirred for three minutes, and then titrated with sulphuric acid, using methyl-orange as indicator. The sulphuric acid is standardised previously against pure mercury fulminate. Any antimony sulphide which may be present is then collected on a filter, washed, dried, and weighed, or estimated volumetrically if the sample contains powdered glass. To the filtrate are added 100 c.c. of 10% ferrous sulphate solution containing 1 c.c. of free sulphuric acid, the mixture is boiled for thirty minutes, the mercury sulphide collected, dissolved in aqua regia, the solution neutralised with ammonia, acidified with hydrochloric acid, and the mercury precipitated as sulphide. The mercury sulphide is collected and weighed, and the filtrate, containing reduced chlorate, is oxidised with nitric acid, and the chloride estimated volumetrically.

W. P. S.

**Preparation of Inorganic Stannichlorides.** J. G. F. DRUCE (*Chem. News*, 1918, **117**, 193—196).—A number of stanno- and stanni-chlorides of uni- and bi-valent metals have been prepared. The stannochlorides were obtained by crystallisation of acid solutions containing stannous chloride and the chloride of the second metal. To obtain the stannichlorides, these solutions were first subjected to the action of chlorine. The recorded analyses of the products, in which the water of crystallisation was obtained by difference, show that magnesium and zinc yield anhydrous stannochlorides, whilst those formed by potassium and ammonium contain two molecules of water of crystallisation. The data for the stannichlorides correspond with the following formulæ: $Li_2SnCl_6,8H_2O$; $Na_2SnCl_6,6H_2O$; $K_2SnCl_6$; $Rb_2SnCl_6$; $(NH_4)_2SnCl_6$; $CaSnCl_6$; $SrSnCl_6,4H_2O$; $MgSnCl_6,6H_2O$; $ZnSnCl_6,6H_2O$; $CdSnCl_6$; $CoSnCl_6,6H_2O$; $NiSnCl_6,6H_2O$.

The anhydrous potassium, rubidium, and ammonium stannichlorides are quite stable in the air and do not deliquesce. The alkaline earth stannochlorides are entirely deliquescent, and on this account it was found impossible to obtain a pure specimen of the barium salt.

H. M. D.

**Normal Zirconyl Nitrate.** ED. CHAUVENET and (MLLE.) L. NICOLLE (*Compt. rend.*, 1918, **166**, 781—783).—The authors were unable to confirm the existence of a normal zirconium nitrate, $Zr(NO_3)_4,5H_2O$, commonly described in text-books. By evaporating a solution of zirconium hydroxide in nitric acid, even in an atmosphere saturated with nitric acid fumes, they always obtained a zirconyl nitrate, $ZrO(NO_3)_2,2H_2O$, or at temperatures below 10° the *hydrate*, $ZrO(NO_3)_2,3{\cdot}5H_2O$. Attempts to prepare the anhydrous nitrate were not successful, the dehydration being always accompanied by loss of nitric acid.

W. G.

**Basic Zirconyl Nitrates.** ED. CHAUVENET and (MLLE.) L. NICOLLE (*Compt. rend.*, 1918, **166**, 821—824).—Zirconyl nitrate, $ZrO(NO_3)_2,2H_2O$ (compare preceding abstract), when dissolved in water, slowly undergoes hydrolysis, and there is slow formation of a precipitate having the composition $ZrO(NO_3)_2,ZrO_2,nH_2O$. A study of the neutralisation by $N/100$-sodium hydroxide of the nitric acid formed during the hydrolysis showed that there are two reactions, namely,

$$2ZrO(NO_3)_2 + 2NaOH = 2NaNO_3 + ZrO(NO_3)_2,ZrO_2 + H_2O$$

and $ZrO(NO_3)_2 + 2NaOH = 2NaNO_3 + ZrO_2 + H_2O$.

When the normal zirconyl nitrate is heated at 120° in the presence of nitric acid vapour, it undergoes dehydration, and at the same time loss of nitric acid, giving a *basic nitrate*, $3ZrO(NO_3)_2,ZrO_2,7H_2O$. If the dehydration takes place in air, there are formed the following basic nitrates: at 110°, $2ZrO(NO_3)_2,ZrO_2,7H_2O$; at 150°, $ZrO(NO_3)_2,2ZrO_2,4H_2O$; at 215°, $ZrO(NO_3)_2,7ZrO_2,5H_2O$; and at 250°, $ZrO(NO_3)_2,10ZrO_2,4H_2O$, and above this temperature zirconium oxide is formed. W. G.

**The Resistance Limits of Mixed Crystals of Vanadium and Silicon with Iron.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 161—179; from *Chem. Zentr.*, 1918, i, 510).—The "resistance limit" is the term given to the composition of mixed crystals at which a sudden alteration occurs in the susceptibility to chemical agents. Whereas it is possible to observe in a direct manner the alterations in the surface of polished pieces of alloys consisting of copper–gold or silver–gold mixed crystals, this cannot be done in the present case, and it is necessary to observe, instead, the effect of various reagents on the metal. After ordinary, slow cooling, mixed crystals of iron and vanadium containing up to 0·43% molecule of the latter are ferromagnetic, whilst mixed crystals richer in vanadium are inactive. Examination was made of the behaviour of the mixed crystals towards solutions of various salts and acids, the resistance limit being found at 0·50 ± 0·05 mol. vanadium.

The iron–silicon mixed crystals gave rather irregular results; solutions of metallic nitrates cause the iron in the mixed crystals to become passive; the action of acids is also somewhat abnormal; copper sulphate, mercuric chloride, gold chloride, and several other salts, together with iodine, indicate a resistance limit at 0·25 mol. silicon, which appears to confirm the existence of the compound FeSi. D. F. T.

## Mineralogical Chemistry.

**The Old and the New Mineralogy.** Sir HENRY ALEXANDER MIERS (T., 1918, **113**, 363—386).—A lecture delivered before the Chemical Society on April 18th, 1918. H. M. D.

**Chemical Composition of Melanophlogites.** E. MANZELLA (*Ann. Chim. Applicata*, 1918, **9**, 91—101. Compare Lasaulx, this Journal, 1876, ii, 54; Bertrand, A., 1881, 1000).—Melanophlogite, a mineral discovered by Lasaulx in association with certain specimens of sulphur, is characterised by its behaviour on heating, changing successively in colour to greyish-yellow, greyish-blue, and deep bluish-black. Purified specimens of various origin recently examined had the following composition: hydrogen, 1·47 to 1·56; carbon, 3·32 to 3·91; silica, 88·76 to 89·12 sulphuric anhydride, 0·63 to 2·49; iron and loss, 0·27 to 0·60; and substances undetermined, 2·67 to 4·94%. A decrease in the proportion of sulphuric anhydride was accompanied by a reduction in the degree of blackening on heating, but other experiments showed that the alteration in colour must be attributed solely to carbonisation of the organic constituents in the mineral. C. A. M.

## Analytical Chemistry.

**Acidimetry of Coloured Solutions. An Application of the Pocket Spectroscope.** ALFRED TINGLE (*J. Soc. Chem. Ind.*, 1918, **37**, 117; *J. Amer. Chem. Soc.*, 1918, **40**, 873—879).—A method is described whereby highly coloured acid solutions may be accurately titrated. The process depends on the fact that the absorption spectra of indicators are different in acid and in alkaline solutions. To make a determination, two similar vessels are taken, one of which contains the solution to be titrated and the other an equal volume of distilled water. To the latter, one drop of standard alkali is added, and then the indicator is slowly added from a burette until the characteristic absorption band shows a sufficiently sharp edge. The position of this edge is noted. Then the same volume of indicator is added to the solution to be estimated, and alkali added from a burette until the characteristic band is observed in the same position. This gives the end-point of the titration. The change does not involve the appearance of a new absorption band, but rather the shifting of a band already present. The method was tested on solutions of sulphuric acid of known concentration, which were coloured by the addition of neutral tea extract or liquorice. The results are quite as accurate as those obtained for colourless solutions by the ordinary method. The amount of indicator used is rather larger than that generally employed; the exact amount necessary must be found experimentally. In the present experiments, 1 c.c. of methyl-orange and 2·5 c.c. of cochineal extract were used. J. F. S.

**Mercuric Oxide as a Standard for Volumetric Analysis.** L. ROSENTHALER (*Zeitsch. anal. Chem.*, 1918, **57**, 98).—Incze has recommended the use of yellow mercuric oxide as a standard in volumetric analysis (A., 1917, ii, 327), but the author points out that he and Abelmann had previously used mercuric oxide for the purpose (A., 1913, ii, 786). W. P. S.

**Detection of Anions.** FRITZ FEIGL (*Zeitsch. anal. Chem.*, 1918, **57**, 135—138).—The substance is boiled with concentrated sodium carbonate solution or fused with a mixture of sodium and potassium carbonates; after filtration, the solution is nearly neutralised with nitric acid and warmed with the addition of an excess of solid zinc nitrate. The mixture is filtered; the precipitate contains zinc sulphide, sulphite, phosphate, borate, fluoride, ferrocyanide, ferricyanide, and cyanide, and also molybdate, vanadate, and tungstate, whilst the filtrate contains zinc thiocyanate, chloride, bromide, iodide, sulphate, thiosulphate, and sulphite. These substances are then identified by drop reactions without further separation. [See also *J. Soc. Chem. Ind.*, July.] W. P. S.

**Estimation of Chlorine in Organic Substances (Gastric Juice, Blood, Milk, etc.).** SIROT and JORET (*Ann. Chim. anal.*, 1918, **23**, 109—113).—The total chlorine in gastric juice is estimated by Volhard's method after the sample has been treated with Esbach's reagent (10 grams of picric acid and 25 grams of acetic acid per litre of water) and filtered. Chlorine in organic and inorganic combination is estimated in the same way after the sample has been evaporated to expel free hydrochloric acid, whilst chlorine in inorganic combination is obtained by titrating the residue left after evaporation and incineration. In the case of blood, sodium metaphosphate is recommended as a clarifier; 20 c.c. of the blood are mixed with 75 c.c. of water, 10 drops of nitric acid, 20 c.c. of 5% sodium metaphosphate solution, and 1·5 c.c. of acetic acid. The mixture is then diluted to 200 c.c., filtered, and the chlorine titrated in the filtrate. The acetic acid–picric acid solution may be used for precipitating the casein, etc., in milk previous to the estimation of the chlorine present. W. P. S.

**Gravimetric Analysis. V. [Chlorides, Bromides, and Iodides.]** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 101—103).—Chlorides, bromides, and iodides are precipitated by a small excess of *N*-silver nitrate in 100 c.c. of the cold solution to which has been added 5 c.c. of *N*-nitric acid, or, in presence of ferric salts, 10—20 c.c. In the case of chlorides and bromides, the mixture is left for one hour and then boiled; in the case of iodides, the silver is added first, the nitric acid after half an hour, and the mixture is boiled after another half-hour. Twenty-four hours later, the precipitate is collected on a plug of cotton wool in a Kelch funnel and dried at 132°. It is washed with 50 c.c. of water acidified with nitric acid, and later with 50 c.c. acidified with acetic acid. Correction values amounting to a few tenths of a mg., according to the weight of the precipitate, are used to improve the accuracy of the results. Iodides may also be precipitated in the presence of hydrochloric acid as palladium iodide. 0·5 Gram of palladium is dissolved in nitric acid and the solution evaporated to dryness several times with hydrochloric acid; the residue is taken up with 10 c.c. of 10% hydrochloric acid, 1 c.c. of alcohol is added to remove any free chlorine, and the solution made up to 100 c.c. In absence of chlorides, the palladium iodide remains in colloidal solution; when precipitated cold, it is flocculent, and becomes granular on heating. With a preponderating quantity of iodide, the neutral solution is diluted so that 100 c.c. will give about 0·1 gram of precipitate; 1·0 gram of sodium chloride is added, and 10 c.c. of palladium chloride solution, with agitation. The liquid is heated until the precipitate becomes granular, and the latter is collected on the cotton filter after twenty-four hours, washed with 100 c.c. of cold water, and dried at 132°. With small quantities of iodide, 100 c.c. of the liquid are acidified with hydrochloric acid and precipitated with 1 c.c. of the palladium solution in the cold. The precipitate is allowed to remain for twenty-four or forty-eight hours, according to its quantity, and is collected in the flocculent condition. The palladium iodide is somewhat soluble in presence of alkali bromides; in presence of large quantities of chlorides, a small correction is applied. J. F. B.

**Titration Method for Chlorine, Bromine, Cyanogen, and Mercury.** Emil Votoček (*Chem. Zeit.*, 1918, **42**, 257—260).—Chlorides may be titrated with standardised mercuric nitrate solution in the presence of a small quantity of nitric acid; 0·06 gram of crystallised sodium nitroprusside is used as the indicator, and the volume of the solution should be about 250 c.c. Sulphates, phosphates, and chlorates do not interfere, but sulphites and nitrites must not be present. The method is trustworthy and more accurate than Volhard's method. [See further, *J. Soc. Chem. Ind.*, July.] W. P. S.

**The Estimation and Distribution of Bromine in the Organs and in the Blood after Dosing with Sodium Bromide.** W. Autenrieth (*Münch. med. Woch.*, 1918, **65**, 33—35; from *Chem. Zentr.*, 1918, i, 472—473).—Bromine in bromides of the alkali metals can be estimated colorimetrically by treating the acidified aqueous solution with potassium hydrogen sulphate and potassium permanganate, the liberated bromine being extracted with chloroform and the extract compared with a standard bromine solution, using the Autenrieth-Königsberger colorimeter. The method is not affected by the presence of chlorine and is especially suitable for small quantities. Organs such as liver, kidneys, brain, etc., are heated in a nickel crucible with pure sodium hydroxide and a little potassium nitrate, and the acidified solution treated in the manner described. Sodium bromide is retained tenaciously by the human organism, and only very slowly eliminated by the kidneys, its retention being favoured by a diet poor in chlorine. The brain shows no specific attraction for bromine. D. F. T.

**Gravimetric and Volumetric Estimation of Fluorine Precipitated as Thorium Fluoride.** F. A. Gooch and Matsusuke Kobayashi (*Amer. J. Sci.*, 1918, [iv], **45**, 370—376).—Investigation of the method described by Pisani (A., 1916, ii, 393) showed that the acidity of the solution and the excess of precipitant are important factors in the estimation of fluorine as thorium fluoride. The acidity of the solution (as free acetic acid) should be from $N/50$ to $N/5$, and the quantity of thorium added should not exceed by more than 50% the amount required for the precipitation. The thorium fluoride may be collected and ignited to oxide, the latter being taken as a measure of the thorium fluoride, $ThF_4,4H_2O$, or the excess of thorium, after filtration, may be precipitated as oxalate and this titrated with permanganate solution (compare this vol., ii, 177). [See, further, *J. Soc. Chem. Ind.*, 391A.] W. P. S.

**Time as a Factor in Gravimetric Analysis. I. Precipitation of Sulphuric Acid.** Z. Karaoglanow (*Zeitsch. anal. Chem.*, 1918, **57**, 77—98).—In the precipitation of sulphuric acid as barium sulphate, the rate at which the barium chloride solution is added has a considerable influence; the most trustworthy results are obtained when the addition is extended over a period of not less than 1·5 minutes. The concentration of the solutions, stirring, concentration of hydrochloric acid, etc., also have an influence, but temperature has little effect. The presence of potassium chloride decreases the amount of barium sulphate found, and to some extent counterbalances the effect of rapid precipitation, but this compensation depends on definite conditions of experiment. W. P. S.

**The Estimation of Sulphates in Urine.** A. L. Flohr (*Arch. Néerland. physiol.*, 1918, **2**, 346—351).—The benzidine method of Rosenheim and Drummond for estimating inorganic and ethereal sulphates gives satisfactory results. If the liquid becomes coloured after hydrolysis of the ethereal sulphates by hydrochloric acid, and the colour interferes with the titration, it can be removed sufficiently by treating the liquid with animal charcoal. S. B. S.

**Estimation of Non-protein Nitrogen in Blood.** Isidor Greenwald (*J. Biol. Chem.*, 1918, **34**, 97—101).—A full account of work previously published (A., 1917, ii, 523). H. W. B.

**New Method for the Direct Nesslerisation of Ammonia in Urine.** James B. Sumner (*J. Biol. Chem.*, 1918, **34**, 37—41).—In the Folin and Denis direct Nesslerisation method (A., 1916, ii, 574), the Merck's blood charcoal may be replaced by copper sulphate. The urine is treated with a practically saturated solution of copper sulphate (298 grams of the crystallised salt per litre). Copper hydroxide is then precipitated by adding a 2·03$N$-sodium hydroxide solution until the neutral point is almost reached, when about 90% of the creatinine is also precipitated. The small amount of creatinine remaining in solution is not sufficient to interfere with the subsequent Nesslerisation.

For rough comparative tests, standard colours similar to those obtained by Nesslerisation are prepared by dilution of a solution containing 6% of crystallised ferric chloride and 2·5% of crystallised cobalt nitrate. H. W. B.

**Apparatus for the Estimation of Nitric Acid by the Schulze-Tiemann Method.** Karl Leuchs (*Chem. Zeit.*, 1918, **42**, 235).—The decomposition flask is closed with a glass stopper provided with a tapped funnel and a delivery tube, and the stopper is surrounded by a water-seal. The delivery tube, which is bent downwards and under the lower end of the gas-collecting burette, is provided with a glass non-return valve. The whole apparatus is constructed of glass. W. P. S.

**Gasometric Estimation of Nitrates.** C. A. Hill (*Analyst*, 1918, **43**, 215—216).—When an external reaction bottle is used in the estimation of nitrates by shaking the latter with sulphuric acid and mercury, it is necessary to fill the bottle previously with a gas inert towards nitric oxide. Carbon monoxide may be used for this purpose, and is prepared by heating a mixture of sodium formate and concentrated sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, July.] W. P. S.

**New Volumetric Method for the Estimation of Phosphates in Urines.** Argeo Angiolani (*Giorn. Farm. Chim.*, 1917, **66**, 251—252; from *Chem. Zentr.*, 1918, i, 571).—Twenty-five c.c. of the urine are treated with 1 c.c. of 20% hydrochloric acid, 1 gram of ammonium chloride, and 10 c.c. of a citric acid–magnesium solution (a solution of 35 grams of magnesium oxide in 260 grams of citric acid, the total bulk being 500 c.c., which is then treated with 400 c.c. of 10% ammonia solution and kept for two hours). The precipitate is collected, washed with very dilute ammonia solution, dried at 30—40°, and then dissolved in 50 c.c. of $N/10$-sulphuric acid, of which the excess is then titrated with $N/10$-sodium hydroxide solution, using methyl-orange as indicator. One c.c. of $N/10$-acid is equivalent to 3·55 mg. $P_2O_5$. D. F. T.

**Marsh's Apparatus.** W. Kirkby (*Pharm. J.*, 1918, **100**, 286).—A tube loosely packed with cotton wool is interposed between the generating flask and the hydrogen jet with the object of preventing any risk of explosion. C. A. M.

**Simple Process for the Estimation of Small Quantities of Arsenic in Corpses.** H. Fühner (*Ber. Deut. Pharm. Ges.*, 1918, **28**, 221—229).—The process consists in the destruction of the animal matter by permanganate and sulphuric acid, the distillation of the solution with sodium chloride, and the estimation of the arsenic in the distillate by the Gutzeit method, using mercuric bromide paper. [See *J. Soc. Chem. Ind.*, July.] J. H. J.

**Estimation of Carbon Dioxide in Carbonates by Dittrich's Method.** BÉLA VON HORVATH (*Chem. Zeit.*, 1918, **42**, 121).—Carbon dioxide may be estimated in sodium carbonate or barium carbonate by heating the same at dull redness with borax which has been heated previously at 1000°; the carbonate is decomposed readily, and the loss in weight gives the amount of carbon dioxide present. [See, further, *J. Soc. Chem. Ind.*, 369A.] W. P. S.

**Filtration of Silica.** P. NICOLARDOT and J. KOENIG (*Ann. Chim. anal.*, 1918, **23**, 104—109).—The fact that a minute quantity of silica passes into the filtrate when hydrated silica is evaporated to dryness and then collected on a filter does not appear to be due to solubility of the silica; the effect of successive evaporations and heating at 110° is to agglomerate the silica so that the whole of it is retained by a good filter. It is recommended that the silica be twice evaporated with hydrochloric acid and heated at 110°, but without intervening filtration, before it is collected; the filtrate may be passed once more through the filter. [See, further, *J. Soc. Chem. Ind.*, July.] W. P. S.

**Estimation of Strontium.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 80 and 83—84).—*As Sulphate.*—One hundred c.c. of a neutral solution containing 0·5 gram of strontium salt are acidified with 1 c.c. of acetic acid, heated to the boiling point, and 10 c.c. of a 10% solution of sodium sulphate are added. Heating is continued until the precipitate is powdery, when it is left overnight. It is transferred to a Gooch crucible, washed with 50 c.c. of saturated strontium sulphate solution, and weighed after drying at 132°. If the filtrate is required further, alcohol is used as the washing agent. The presence of other salts, especially magnesium chloride and hydrochloric and nitric acids, leads to low results.

*As Carbonate.*—1·0 Gram of potassium nitrate and 10 c.c. of 10% sodium carbonate solution are added to a boiling solution of not more than 0·5 gram of strontium salt in 100 c.c. of solution. Next day the precipitate is washed with 50 c.c. of saturated strontium carbonate solution and weighed as $SrCO_3$ after drying at 132°. Owing to incomplete loss of carbon dioxide on ignition, the precipitate cannot be weighed as oxide.

*As Oxalate.*—The precipitation is made with 10% solution of potassium oxalate, and resembles that of the sulphate. After remaining overnight, the precipitate is washed with saturated strontium oxalate solution. It is dried at 100° for two hours and weighed as $SrC_2O_4,H_2O$, or at 132° for six hours and weighed as $SrC_2O_4$. Other salts, especially magnesium chloride, interfere. This is the most convenient and exact method of estimating strontium. H. J. H.

**Time as a Factor in Gravimetric Analysis. Precipitation of Barium Chloride with Sulphuric Acid.** Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1918, **57**, 113—121).—In the gravimetric estimation of barium as barium sulphate, sulphuric acid should be used for the precipitation; alkali sulphates must not be used. The acid should be added rapidly; if it is added slowly, the results obtained are too low. [See, further, *J. Soc. Chem. Ind.*, 352A.] W. P. S.

**Volumetric Estimation of Lead by means of Ammonium Molybdate.** LINDT (*Zeitsch. anal. Chem.*, 1918, **57**, 71—76).—In this process, it is essential that an excess of ammonium acetate should be avoided in dissolving the lead sulphate; the results obtained are too high in the presence of such excess, but are trustworthy when the lead sulphate is dissolved in the minimum requisite quantity of the acetate solution. [See, further, *J. Soc. Chem. Ind.*, 352A.] W. P. S.

**Estimation of Copper as Copper Oxide after previous Precipitation as Thiocyanate.** G. FENNER and J. FORSCHMANN (*Chem. Zeit.*, 1918, **42**, 205—206).—The inconvenient drying of the cuprous thiocyanate precipitate to constant weight is unnecessary, and may be avoided by conversion of the precipitate into cupric oxide by roasting in a muffle at a temperature near 800°. [See also *J. Soc. Chem. Ind.*, 391A.] D. F. T.

**Analysis of White Metal.** F. KUREK and A. FLATH (*Chem. Zeit.*, 1918, **42**, 133—134).—Tin is estimated by dissolving the alloy in hydrochloric acid with the addition of ferric chloride, reducing the tin with metallic iron, separating the precipitated antimony and copper, and titrating the filtrate with ferric chloride solution. The antimony and copper are then dissolved in hydrochloric acid to which potassium chlorate is added, excess of free chlorine is expelled by boiling the solution, the two metals are separated as their sulphides, the antimony sulphide is dissolved in sodium sulphide solution, again precipitated in the presence of an excess of oxalic acid, dissolved in hydrochloric acid, the solution boiled until the antimony is reduced, and then titrated with potassium bromate solution. Suitable methods are also described for the estimation of lead, copper, iron, aluminium, nickel, and zinc in the alloy. [See, further, *J. Soc. Chem. Ind.*, 877A.) W. P. S.

**Use of Metallic Silver as a Reducing Agent in the Volumetric Estimation of Iron.** GRAHAM EDGAR and A. R. KEMP (*J. Amer. Chem. Soc.*, 1918, **40**, 777—784).—The reaction between metallic silver and solutions of ferric sulphate in the presence of sulphuric acid and a soluble thiocyanate has been examined. The results obtained show that silver may be employed to effect the complete reduction of the ferric salt provided the dissolved silver is precipitated by thiocyanate. The resulting ferrous solution is filtered, treated with an excess of silver nitrate, and titrated with potassium permanganate. An alternative method consists in titrating the excess of silver nitrate with standard thiocyanate.

The thiocyanate serves to show when the reduction is complete, and further advantages of the method are that silver is usually quite free from iron, that it does not reduce titanium at all, and that it reduces vanadium quantitatively to the quadrivalent condition. [Compare *J. Soc. Chem. Ind.*, 391A.] H. M. D.

**Estimation of Iron in Lactic Acid.** A. HARVEY (*J. Soc. Leather Trades' Chem.*, 1918, **2**, 37—38).—Iron in lactic acid can be estimated very exactly by a colorimetric method in which the colour developed with potassium ferrocyanide is matched against the colour produced by standard iron solution. Potassium thiocyanate is useless. F. C. T.

**Quantitative Separation of Iron from the Cerite Metals in the presence of Calcium.** A. WÖBER (*Zeitsch. landw. Versuchsw. Oesterr.*, 1917, **20**, 500—501; from *Chem. Zentr.*, 1918, i, 476).—A weighed sample is dissolved by prolonged treatment with 2% hydrochloric acid, and to an aliquot portion of the solution there is added tartaric acid in the proportion of approximately four grams to one of the substance. On saturating the solution with hydrogen sulphide and adding aqueous ammonia until a pure black precipitate of iron sulphide is obtained, the transiently precipitated hydroxides of the cerite metals are redissolved. The iron sulphide is treated in the usual manner, whilst the estimation of the cerite metals is effected by the method of Hauser and Wirth (A., 1908, ii, 778). D. F. T.

**Estimation of Nickel with α-Benzildioxime.** R. STREBINGER (*Chem. Zeit.*, 1918, **42**, 242—243).—The author agrees with Grossmann and Mannheim (A., 1917, ii, 391) that Atack's method of estimating nickel by precipitation with α-benzildioxime is trustworthy for small quantities of the metal. When, however, the quantity of nickel exceeds 0·025 gram, the precipitate contains a certain amount of occluded α-benzildioxime, and the results obtained are too high. In such cases, the precipitate should be ignited and the resulting nickel oxide weighed. W. P. S.

**Estimation of Chromium in Chromium Salts, Chrome Liquors, Leather Ashes, and Chromium Residues.** KARL SCHORLEMMER (*Collegium*, 1917, 345 and 371; from *Chem. Zentr.*, 1918, i, 377—378).—The solution of the chromium salt is treated cautiously with approximately *N*-sodium hydroxide until the precipitate has redissolved. Aqueous hydrogen peroxide of approximately 3% concentration is then added, and the solution is boiled until no more oxygen is liberated. The resulting solution is acidified with sulphuric acid, and the amount of chromate estimated by one of the usual volumetric methods. Leather ash or dry chromium residues should be mixed with anhydrous sodium carbonate and magnesium oxide and roasted until yellow, the aqueous extract then being titrated after acidification. For the oxidation of solutions of very impure chromium salts, it is better to use alkaline potassium permanganate solution. The presence of iron in the ash of chrome leather may interfere with the chromium estimation. D. F. T.

**Estimation of Molybdenum.** O. BINDER (*Chem. Zeit.*, 1918, **42**, 255).—When molybdenum is precipitated as sulphide and the latter then ignited to oxide, the oxidation is not complete unless the substance, after preliminary ignition, is treated with nitric acid, evaporated, dissolved in ammonia, reprecipitated with nitric acid, evaporated, and ignited. A correction must be made for any traces of matter which remain insoluble when the ignited oxide is dissolved in ammonia. [See, further, *J. Soc. Chem. Ind.*, July.] W. P. S.

**The Estimation of Molybdenum as Lead Molybdate.** ROBERT STREBINGER (*Oesterr. Chem. Zeit.*, 1917, [ii], **20**, 226—228; from *Chem. Zentr.*, 1918, i, 378).—For the estimation of molybdenum in ferro-molybdenum, 0·5—1 gram is fused with 10 grams of sodium peroxide in an iron crucible. The product is extracted with 500 c.c. of water, and 100 c.c. are taken for the test; after the removal of any iron by the addition of nitric acid and then ammonia solution, the solution is neutralised with acetic acid, boiled, and treated successively with solutions of lead acetate (2—5 grams) with acetic acid (2 c.c.) in 30 c.c. of water, and ammonium acetate (10 grams) in 50 c.c. of water. After boiling for a short time, the precipitate is allowed to settle for six hours. The precipitate is removed by filtration, washed with dilute ammonium acetate solution, dissolved in diluted nitric acid, and reprecipitated by the addition of a solution of ammonium acetate (10 grams) in 50 c.c. of very dilute acetic acid. After twelve hours, the lead molybdate is again separated, washed, dried, and ignited at a moderate temperature before final weighing as $PbMoO_4$. D. F. T.

**A Colour Reaction of Thorium and Zirconium with Pyrogallolaldehyde.** H. KASERER (*Chem. Zeit.*, 1918, **42**, 170).—On the addition of an aqueous solution of pyrogallolaldehyde to one of a thorium compound, a yellow colour is formed, and, after a time, a dirty yellow precipitate is produced, which when filtered off leaves a colourless filtrate. Zirconium compounds, after boiling or after the addition of hydrogen peroxide, give a similar colour and precipitate with cerium compounds; the yellow colour remains after boiling. In the presence of nitric, sulphuric, or hydrochloric acid, a colourless solution and no precipitate are produced. A solution containing only 0·1 mg. of thorium nitrate per 100 c.c. shows the colour clearly. Pyrogallol, pyrogallolcarboxylic acid, and protocatechualdehyde do not give this reaction.

The pyrogallolaldehyde is prepared by dissolving 38 grams of pyrogallol and 36·3 grams of formanilide in absolute ether, condensing this with 15·2 grams of phosphoryl chloride, and filtering after twelve hours. The residue is dissolved in alcohol and precipitated by sodium chloride. The crystals are treated with warm sodium hydroxide, a current of hydrogen is passed through the solution, after which it is acidified and the aldehyde extracted with ether and purified by conversion into the bisulphite compound.

A. B. S.

**Graphic Methods of Analysis.** HANS GRADENWITZ (*Chem. Zeit.*, 1918, **42**, 221).—The composition of such mixtures as formaldehyde, methyl alcohol, and water, and ethyl acetate, alcohol, and water, may be found from the graphs given, the data to be determined being, in the first case, the specific gravity and the formaldehyde content, and in the second, the specific gravity and the ethyl acetate content. [See, further, *J. Soc. Chem. Ind.*, 392A.]

W. P. S.

**Method for Detecting Small Quantities of Chloretone (Trichloro-*tert.*-butyl Alcohol) in Aqueous Solutions.** T. B. ALDRICH (*J. Biol. Chem.*, 1918, **34**, 263—267).—The solution containing the chloretone is subjected to steam distillation. If a large amount of chloretone is present, it crystallises in the cooler part of the condenser in needles. When only small amounts of chloretone are present, crystallisation may not occur, but if the distillate is placed in a small flask fitted with a reflux condenser and boiled for half an hour, needle crystals are then obtained in the condenser when the amount of chloretone exceeds 0·25 mg. If protein is present, it should be digested with pepsin and hydrochloric acid before the steam distillation is carried out. The presence of other organic solvents prevents the crystallisation, and thus interferes with the recognition of chloretone by this method.

H. W. B.

**Estimation of Cholesterol in Blood.** L. KAST, V. C. MYERS, and EMMA L. WARDELL (*Proc. Soc. Exp. Biol. Med.*, 1917, **15**, 1—2; from *Physiol. Abstr.*, 1918, **3**, 31).—One c.c. of blood is extracted with chloroform, and in the extract the cholesterol is estimated colorimetrically by the Liebermann-Burchard reaction (compare *Physiol. Abstr.*, 1917, **2**, 675). The values obtained are lower than those of Bloor, but are believed to be more accurate.

W. G.

**Cammidge's Method for the Estimation of [Reducing] Sugar in Urine.** R. W. GARROW (*Pharm. J.*, 1918, **100**, 148—149).—In estimating sugar by this method (A., 1917, ii, 276), it is noticed in titrating back the excess of iodine with thiosulphate that up to the point where the blue starch iodide is discharged the solution is transparent, but immediately after the first end-point is reached a slight opalescence begins to appear, in-author describes a method whereby silver solutions may be titrated with iodide in the presence of such metals and in very dilute solution by use of a solution of palladous nitrate as indicator. The indicator is prepared by dissolving 0·06% of palladous nitrate in 16% nitric acid; it is found advisable to use a protective colloid along with the indicator to prevent the occlusion of potassium iodide or silver nitrate. For this purpose, a 5% solution of gum arabic is found most advantageous. The indicator is converted by the first excess of iodide into palladous iodide, which gives a red colour to the solution; this action is sensitive to 1 part in 500,000. This method is further to be recommended on account of the accuracy and easy reproducibility with both *N*/10- and *N*/1000-solutions. The author discusses at some length the possible errors of the method, and gives full details of the procedure to be adopted for *N*/10- and *N*/1000-solutions. J. F. S.

**Field Methods for the Determination of the Total Hardness of Water.** A. S. BEHRMAN (*Philippine J. Sci.*, 1918, **13**, [A], 21—27).—Blacher's method of titration with potassium palmitate has been adapted to field conditions. The water is titrated with standard pellets of the reagent. [See, further, *J. Soc. Chem. Ind.*, June.] H. J. H.

**Analysis of Glass.** L. RONNET (*Ann. Falsif.*, 1918, **11**, 26—31).—A scheme is given for the analysis of glass containing silica, iron, aluminium, manganese, calcium, magnesium, potassium, and sodium. The usual methods of separating and estimating these constituents are employed. [See, further, *J. Soc. Chem. Ind.*, 1918, 266A.] W. P. S.

**Estimation of the Reducing Power of Urine, both free from and containing Dextrose, by means of an Alkaline Glycerol-Copper Solution.** H. RUOSS (*Zeitsch. physiol. Chem.*, 1918, **101**, 131—164).—The method previously described (A., 1917, ii, 549) is modified by employing a glycerol–copper solution and by using always the same volume of urine with varying quantities of copper solution instead of maintaining a constant volume of the latter and varying the former. The glycerol–copper solution is prepared by dissolving 3·464 grams of copper sulphate in 10 c.c. of hot water, cooling, and adding 15 c.c. of glycerol and 22 c.c. of sodium hydroxide solution (D 1·357). The mixture is again cooled, 5 c.c. of a 30% potassium thiocyanate solution added, and then the volume brought to 100 c.c. by the addition of 25% sodium chloride solution. For an estimation, 5 c.c. of urine are treated with from 0·1 to 1 c.c. of the new reagent, and, after boiling, the end-point determined in the manner previously described (*loc. cit.*). The amount of copper solution is varied until it is exactly reduced by the dextrose or other reducing substances present in the urine.

Attention is directed to the fact that the reducing power of urine free from sugar is proportional to $D-1$, where $D$ is the specific gravity of the urine, and that the urine may be freed from substances containing nitrogen by treatment with an excess of the Patein-Schöndorff mercuric nitrate reagent (A., 1908, ii, 311), the excess of mercury being subsequently removed by precipitation with alkali followed by zinc dust. H. W. B.

**Copper-Phosphate Mixtures as Sugar Reagents. A Qualitative Test and a Quantitative Titration Method for Dextrose in Urine.** OTTO FOLIN and W. S. MCELLROY (*J. Biol. Chem.*, 1918, **33**, 513—519).—The qualitative reagent is prepared by dissolving 100 grams of sodium pyrophosphate (U.S.P.), 30 grams of crystallised disodium hydrogen phosphate, and 50 grams of anhydrous sodium carbonate in about a litre of water, and adding 13 grams of copper sulphate previously dissolved in about 200 c.c. of water. The solution appears to keep indefinitely and is cheaply prepared. To test for reducing sugars, 5 c.c. of the reagent are placed in a test-tube, five to eight drops (not more than 0·5 c.c.) of the urine added, and the mixture boiled for one minute, or heated in boiling water for three to five minutes. Minute traces of sugar are indicated by various grades of turbidity, larger amounts by unmistakable precipitates of cuprous oxide. A slight turbidity occurring after cooling may be due only to the reducing action of normal urine.

For quantitative estimation, the only solution required is an acidified copper sulphate solution containing 60 grams of crystallised copper sulphate and 4 c.c. of concentrated sulphuric acid per litre. Five c.c. of this solution correspond with 25 mg. of dextrose or lævulose, 45 mg. of anhydrous maltose, or 40·4 mg. of anhydrous lactose. The other necessary reagent is a dry mixture containing 100 grams of crystallised disodium hydrogen phosphate, 60 grams of dry sodium carbonate, and 30 grams of sodium or potassium thiocyanate. The authors recommend the titrations to be made in test-tubes, using undiluted urine. This simplification is made possible by attaching to the tip of an ordinary 25 c.c. glass-stoppered burette another tip consisting of a glass tube drawn out at one end to an almost capillary bore, and delivering between forty-five and fifty-five drops of urine per c.c. If the burettes carrying accessory tips are filled by suction, the necessity of rinsing the burette with the sugar solution to be titrated is avoided, which can be proved by filling the burette with water after it has just been emptied from a urine containing 5% of sugar. On testing the water in the lower part of the burette, it is found to be quite free from sugar. To carry out an estimation, 5 c.c. of the copper reagent and 4 to 5 grams of the dry salt mixture are heated in a test-tube until a clear solution is obtained (a pebble is added to prevent bumping). Twenty-five drops of urine are run in from the burette, and the mixture gently boiled for two minutes. If the solution is still blue, more urine is run in, boiling for one minute after each addition, until the solution is colourless. From the total number of drops, the volume of urine added can be computed, and hence the percentage of dextrose in the urine. The results of the titration should be confirmed by a repetition, in which the first addition of urine should be only two or three drops less than the full amount of urine required. The total period of boiling must not be less than four or more than seven minutes.

The presence of albumin in the urine does not obscure the end-point of the titration. The use of the test-tube instead of a flask or beaker greatly retards the reoxidation of the cuprous oxide and materially aids the rapid performance of the test. If desired, a 5 c.c. burette graduated in 0·02 c.c. divisions may be used instead of the ordinary burette with capillary tip described above.

H. W. B.

**Estimation of Lactose in Milk.** Otto Folin and W. Denis (*J. Biol. Chem.*, 1918, **33**, 521—524).—The authors describe two methods, based on titration and colorimetry respectively, the former being considered to give the more nearly accurate results. In the titration method, the reagents and apparatus described for the estimation of dextrose in urine (preceding abstract) are employed, and neither the protein nor the fat is previously removed from the milk. The milk is simply diluted with water (1 : 4) and added directly to the copper-phosphate solution, boiling being continued rather longer than in the estimation of dextrose.

For the colorimetric estimation, a modification of Dehn and Hartman's method (A., 1914, ii, 223) is described which is based on the colour developed when an alkaline solution of lactose in saturated picric acid is heated for a fixed time at 100°. [See, further, *J. Soc. Chem. Ind.*, 278A.]

H. W. B.

**Estimation of Dicyanodiamide in Old Calcium Cyanamide.** H. Kappen (*Zeitsch. angew. Chem.*, 1918, **31**, 31—32).—A sample of very old calcium cyanamide was found to be free from cyanamide nitrogen; the dicyanodiamide nitrogen was estimated by Caro's and by Hager's methods. The results obtained by these two methods did not agree (compare Hager and Kern, A., 1916, ii, 687), and the author suggests that the difference may be due, in part, to the presence of urea in the sample. This is confirmed by the results of analyses of mixtures of urea and dicyanodiamide; urea has less effect on the results obtained by Caro's method than it has on those found by Hager's method.

W. P. S.

**The Spectroscopic-quantitative Estimation of Urochromogen.** Traugott Baumgärtel (*Biochem. Zeitsch.*, 1918, **85**, 162—170).—The author gives a modification of the method of Weiss for the estimation of urochromogen by oxidation with potassium permanganate, in which the colorimetric method adopted by Weiss is replaced by the detection of excess of permanganate spectroscopically. The method has been applied to the determination of the urochromogen output in the urine in certain pathological cases.

S. B. S.

# General and Physical Chemistry.

**Double Refraction and Optical Activity of Liquid-Crystalline Substances.** Felix Stumpf (*Jahr. Radioakt. Elektronik*, 1918, **15**, 1—64).—A useful and detailed résumé, including bibliography, of the work since the earlier résumé in the same journal by R. Schenck in 1909, is given in six chapters, entitled: (1) Double refraction of inactive and active substances. (2) Rotation of plane of polarisation. (3) Theory of uniaxial active absorbing crystals. (4) Observations on the state of polarisation oblique to the axis of the advancing waves. (5) The theory of M. Born and its experimental examination. (6) The action of the magnetic field on liquid-crystalline substances. F. S.

**Anomalous Molecular Distribution in Mixed Crystals as the Cause of their Anomalous Double Refraction.** G. Tammann (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 226—235; from *Chem. Zentr.*, 1918, i, 567).—A consideration as to the cause of the internal strains to which the anomalous optical properties of some mixed crystals have been attributed. It is not very probable that during rapid crystallisation correct distribution of the components can occur completely so that the blending is entirely consistent with the symmetry of the space lattice. The disturbance in the molecular distribution will cause a reduction in the linear velocity of crystallisation and a deviation in the properties of the mixed crystal from those expected from its symmetry; both these effects are frequently observed. If an anomalous mixed crystal represents an unstable system, the solubility should be least for the normal mixed crystal, as has, indeed, been observed. It is calculated that the alteration in solubility to be expected from the effect of the internal strains in a certain case is 0·3%, whereas the observed difference in solubility may attain 50%. According to this result, the abnormal arrangement in the crystal lattice exerts a direct influence, and not merely an indirect effect on account of the internal strains. D. F. T.

**Electrical Double Refraction in Liquids.** C. Bergholm (*Ann. Physik*, 1917, [iv], **54**, 511—518).—The author discusses the question of the dependence of the electrical double refraction on the composition and constitution of organic compounds, and points out that Kerr's constant cannot be considered to offer a suitable basis for the comparison of different substances. In place of Kerr's constant $B$, the quantity $B_R = B\lambda nM/(K+2)^2(n^2+2)^2d$ is proposed, $\lambda$ being the wave-length of the light used, $n$ the ordinary refractive index, $M$ the molecular weight of the substance, $K$ the dielectric constant, and $d$ its density. The quantity $54B_R$ represents the "electrical double refraction of the molecular refraction" for a layer of liquid 1 cm. in thickness and an electrostatic field of unit intensity. The values of $B_R$ for a number of substances are compared, and from this it would seem that in the case of aromatic compounds which have similar absorption spectra, the value of $B_R$ varies but little with the nature of the substituent element or group and its position in the benzene ring.

H. M. D.

**The Light Emission of Gases and Mixtures of Gases by Electric Discharges.** L. Hamburger (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1043—1048).—A summary is given of experiments in which the effect of pressure and of the intensity of the electric discharge on the emission spectra of certain gases and gas mixtures was examined.

The observations made with nitrogen, hydrogen, neon, and helium show that the intensity of the lines and bands is proportional to the energy of the discharge, and that the maximum emission is displaced towards the ultra-violet when the pressure is decreased. Argon behaves quite differently, and the nature of the divergence depends on whether the red or the blue spectrum is emitted. If the intensity is plotted against the strength of the current, curves are obtained which are concave or convex to the current axis, according to whether the red or the blue spectrum is considered.

Observations made on mixtures of non-reactive gases show that there is generally a shift of the maximum towards the ultra-violet which may be interpreted in terms of the pressure effect referred to above. In the case of mixtures of gases which react with each other, the observations show that new bands make their appearance in the discharge spectrum. H. M. D.

**Absorption of Ultra-violet Rays by Phenyl Derivatives of Methane.** G. Massol and A. Faucon (*Compt. rend.*, 1918, **166**, 819—821).—A study of the absorption spectra of benzene, toluene, and di- and tri-phenylmethanes. The results indicate that benzene and the three phenyl derivatives of methane show a general transparency for the radiations extending from the visible spectrum to $\lambda=270$ and a selective absorption for the radiations from $\lambda=270$ to $\lambda=230$. This selective absorption varies with the different compounds, and the characteristic spectrum of benzene with its narrow bands and its undulating aspect is not found in the phenyl derivatives of methane. Their bands are less numerous, often slightly displaced, and do not all appear at the same time. The transparency diminishes as the molecular weight increases. W. G.

**Confirmation of van't Hoff's Hypothesis. Optical Superposition in the Meta-saccharins and Related Substances.** Edwin A. Hill (*J. Amer. Chem. Soc.*, 1918, **40**, 764—773).—The question of the validity of the principle of optical superposition has been examined by reference to the rotatory powers of the four meta-saccharins and of their strychnine, brucine, and quinine salts. It is shown that the specific and molecular rotations may be satisfactorily represented as the algebraic sums of three constants corresponding with the active $\alpha$-, $\gamma$-, and $\delta$-carbon atoms. The calculated constants for the $\alpha$- and $\gamma$-carbon atoms are very nearly the same for all the salts, but differ considerably from the $\alpha$- and $\gamma$-constants for the saccharins themselves. This is quite in accordance with the fact that ring structure is present in the saccharins, whilst the salts are characterised by chain structure. The sum of the activities of the $\delta$-carbon atom and the active base remains constant for the four salts corresponding with each of the three bases, but changes its value with the nature of the alkaloid.

By using the average values of the constants and calculating the specific rotations of the twelve salts, it is found that the average differences between the calculated and observed rotations are 0·94° for the strychnine salts, 0·25° for the brucine salts, and 0·22° for the quinine salts.

Reference is made to other recorded data which afford evidence of the validity of the principle of optical superposition.

H. M. D.

**Action of Light-rays on Organic Compounds and the Photosynthesis of Organic from Inorganic Compounds in Presence of Inorganic Colloids.** Benjamin Moore and T. A. Webster (*Proc. Roy. Soc.*, 1918, [*B.*] **90**, 168—186).—In the formation of formaldehyde from carbon dioxide in light in the presence of an inorganic catalyst, it is shown that the action depends, not only on the specific character of the catalyst, but also on its state of aggregation. Exposure of formaldehyde solutions to light lead to the formation of condensation products which reduce Benedict's solution. The relationship between the osmotic energy and thermochemical relations in reversible reactions of this description is discussed. The authors also discuss generally the formation of formaldehyde by phytochemical decomposition of more complex substances. S. B. S.

**The Parent of Actinium.** Frederick Soddy and John A. Cranston [and, in part, Ada Hitchins] (*Proc. Roy. Soc.*, 1918, [*A.*] **94**, 384—404).—The history of the long search for the parent of actinium, and of the various theories that have been framed to connect it with uranium, is dealt with in full. The present work was undertaken to test the hypothesis that actinium is produced from "eka-tantalum," the missing element between uranium and thorium in the Periodic Table, by its disintegration in a slow $\alpha$-ray change, giving actinium. Eka-tantalum is probably the product of uranium-$Y$, discovered by Antonov (A., 1911, ii, 844; 1914, ii, 17), and it should be isotopic with uranium-$X_2$ or brevium.

It was found that uranium-$X_2$ could be effectively separated from uranium-$X_1$, isotopic with thorium, by distillation at a dull red heat in chlorine charged with carbon tetrachloride vapour, the uranium-$X_2$ volatilising. The attempt was made to separate eka-tantalum from pitchblende similarly. About 500 grams of a very pure Indian pitchblende ($U_3O_8$ 86%, PbO 11·9%, $ThO_2$ 1·9%, $SiO_2$ 0·6%) similarly treated gave three sublimates, the first after twenty-two hours, the second after ninety hours further, and the last [prepared by (Miss) A. Hitchins] after six hours at a much higher temperature. These sublimates were kept under observation for the growth of actinium, from which they were initially free. The presence of actinium was tested for by means of its characteristic active deposit. The second sublimate, in the course of one thousand days, produced a quantity of actinium twenty times greater than could be with certainty detected. So far as can yet be seen, the rate of growth of actinium appears to be linear with the time, pointing to a direct production. The other preparations have remained free from actinium. Another preparation, from Joachimsthal pitchblende, treated similarly, gave a sublimate also giving actinium with time. For the second sublimate from Indian pitchblende, the attempt was made to compare the quantity of actinium present after 2·5 years with that in the originating pitchblende. The amount of actinium present was found to be the same as that in 0·25 gram of the pitchblende. On the assumptions (1) that the actinium is produced in a direct change, (2) that the sublimate contained all the parent of actinium present in the original mineral, the period of average life of actinium is calculated to be 5,000 years. The quantitative measurement by radio-active methods of minute quantities of actinium by means of its emanation and active deposit presents difficulties which have not been completely overcome. The work supports the theory of the origin of actinium, referred to at the beginning, but does not finally establish it to the exclusion of all other possible modes of origin.

F. S.

**Mobilities of Ions in Air, Hydrogen, and Nitrogen.** KIA-LOK YEN (*Proc. Nat. Acad. Sci.*, 1918, **4**, 91—97).—The mobilities of the positive and negative ions in air, hydrogen, and nitrogen have been measured at various pressures and for widely different potentials. The results show that the mobility varies inversely as the pressure, and that the product of these quantities is independent of the strength of the field in the case of both positive and negative ions. The results are discussed with reference to the constitution of the ions, and the author contends that they afford support for the view that the ions consist of a single atom or molecule, as opposed to the cluster hypothesis according to which an ion is supposed to consist of a relatively large group of satellite molecules. The fact that the mobility of the negative ions is in all cases greater than that of the positive ions can be readily explained in terms of the simple ion hypothesis when the relative magnitude of the forces acting between neutral molecules and ions of opposite sign is taken into account. This attractive force is greater for the positive ion, and, in consequence, the effective mean free path of the positive ion is less than that of the negative ion.

The reduced mean free path involves a diminution in the mobility of the positive ions as compared with that of the negative ions.
H. M. D.

**Mobilities of Ions in Vapours.** Kia-Lok Yen (*Proc. Nat. Acad. Sci.*, 1918, **4**, 106—109).—The mobilities of the positive and negative ions in sulphur dioxide, acetaldehyde, ethyl chloride, ethyl alcohol, pentane, acetone, ethyl acetate, ethyl iodide, and methyl iodide have been measured at various pressures. The mean values obtained show that the mobility of the negative ion is slightly greater than that of the positive, except in the case of ethyl iodide, for which the observed values are the same. The ratio of the mobilities of the oppositely charged ions in these vapours is much smaller than the ratio found in the case of air, hydrogen, and nitrogen, and is quite in accordance with the assumption that the ions are simple in type (compare preceding abstract). H. M. D.

**The Distribution of Radioactive Gases in the Free Atmosphere.** Victor F. Hess and Wilhelm Schmidt (*Physikal. Zeitsch.*, 1918, **19**, 109—113).—From the point of view of present knowledge of the interchange going on in the free air by virtue of the random molecular motion, the law for the distribution with height of a radioactive gas in the atmosphere and the comparison of the amount at any altitude with that present at the earth's surface have been worked out. The calculated values agree with such observations as have been made for the radium emanation, so far as the order of magnitude is concerned. The calculated values, for the height in which the quantity of the radioactive material per gram of air is reduced to half the value at the surface, are:

Radium emanation and its short-lived products, about 1200 metres.

Radium-*D* and subsequent products, uniform up to 10 kilometres.

Thorium emanation and thorium-*A*, 2 to 3 metres.

Thorium-*B* and subsequent products, 100 to 150 metres.

Actinium emanation and actinium-*A*, 0·5 to 1 metre.

Actinium-*B* and subsequent products, 10 to 20 metres.

The total quantity of radium emanation in the whole atmosphere is estimated as between 1·6 and $2·3 \times 10^7$ Curies. F. S.

**Attempted Separation of Isotopic Elements by means of Fractional Diffusion.** H. Lachs, M. Nadratowska, and L. Wertenstein (*Compt. rend., Soc. Sci. Warsaw*, 1917, **9**, 670—672; from *Chem. Zentr.*, 1918, i, 416).—In an attempt to separate the isotopes $U_1$ and $U_2$ by the fractional diffusion of a solution of uranyl nitrate, no difference was observable between the radioactivity of the diffusate and of the original substance. If there is any difference between the diffusion coefficients of the two isotopes, it cannot be greater than 1·5%. D. F. T.

**Can the Production of Electricity by Organic Substances and Living Tissue be Explained by known Thermodynamic Laws?** R. Beutner (*Zeitsch. Elektrochem.*, 1918, **24**, 94—100).—Polemical against Baur and Kronmann (A., 1917, ii, 231). It is shown that the production of the current in two-phase liquid elements can be explained thermodynamically, and, consequently, the production of the biological current can also be explained in the same way. It is claimed that the absorption theory of Baur, which is put forward to take the place of the thermodynamic theory, is therefore superfluous, and, furthermore, unproved. J. F. S.

**Can the Production of Electricity by Organic Substances and Living Tissues be Explained by known Thermodynamic Laws?** Emil Baur (*Zeitsch. Elektrochem.*, 1918, **24**, 100—101).—Polemical, an answer to Beutner (see preceding abstract). J. F. S.

**Potentials of the Bismuth–Bismuth Oxychloride and the Copper–Cuprous Chloride Electrodes.** Arthur A. Noyes and Ming Chow (*J. Amer. Chem. Soc.*, 1918, **40**, 739—763).—The normal potentials have been derived from measurements of the *E.M.F.* of cells formed by combination of the bismuth oxychloride and cuprous chloride electrodes with the hydrogen electrode and with each other. The mean values obtained for the normal potential of the bismuth oxychloride electrode are −0·1635, −0·1599, and −0·1563 volt at 15°, 25°, and 35° respectively. The corresponding values for the cuprous chloride electrode are −0·1263, −0·1200, and −0·1132 volt respectively.

From the temperature coefficients of the electrode potentials, the authors have calculated the heat changes accompanying the chemical reactions. The results are expressed in the equations

$$3/2H_2 + 3CuCl = 3Cu + 3\overset{+}{H} + 3\overset{-}{Cl} + 21570 \text{ cal.}$$

$$3/2H_2 + BiOCl = Bi + H_2O + \overset{+}{H} + \overset{-}{Cl} + 18500 \text{ cal.}$$

$$Bi + 3CuCl + H_2O = 3Cu + BiOCl + 2\overset{+}{H} + 2\overset{-}{Cl} + 2825 \text{ cal.}$$

By measuring directly the heat of the reaction between metallic tin and bismuth oxychloride, and also of the reaction between tin and cuprous chloride in presence of dilute hydrochloric acid, the value found for the last of the above reactions is 7390 cal., which is very much larger than that indicated by the potential measurements. The discrepancy has not yet been accounted for.

The equilibrium corresponding with the equation $Bi + 3CuCl + H_2O \rightleftarrows 3Cu + BiOCl + 2\overset{+}{H} + 2\overset{-}{Cl}$ has been determined by experiments at 75°. The constant $K_{75} = [\overset{+}{H}]^2 . [\overset{-}{Cl}]^2$ has the value $2·10 \times 10^{-3}$. H. M. D.

**Electrical Endosmose. II.** T. R. Briggs, H. S. Bennett, and H. L. Pierson (*J. Physical Chem.*, 1918, **22**, 256—272. Compare A., 1917, ii, 236).—An improved form of electro-osmometer is described which consists essentially of a horizontal tube containing the diaphragm, in close proximity to which are the electrodes, which pass through vertical side tubes which permit of the escape of gases generated during the passage of the current. The anode and cathode compartments are also connected through a narrow tube which contains an air bubble. This tube is provided with a scale, and the rate at which the bubble moves along the tube affords a measure of the electro-endosmotic flow.

Measurements have been made which show the dependence of the effect on the applied potential difference, the temperature, and on the nature of the diaphragm and of the dissolved electrolyte.

The rate of endosmotic flow is proportional to the applied difference of potential. For a given potential, it increases with rise of temperature, the rate of increase being somewhat smaller than that of the fluidity.

The results obtained in the investigation of dilute acid and alkaline solutions confirm the observation, made by Perrin, that the direction of flow undergoes reversal on passing from an acid to an alkaline solution. With a carborundum diaphragm, the isoelectric point was found to correspond with a very slightly acid solution. Sharp reversals were also obtained with alundun and also with diaphragms of gelatin and agar jellies. With powdered glass, no reversal was obtained.

Observations made with various copper salts are also recorded, and the bearing of the electro-endosmotic effects on the electrical and adsorption theories of dyeing is discussed in reference to some experiments made with acid and basic dyes. H. M. D.

**The Abnormality of Strong Electrolytes. I. Electrical Conductivity of Aqueous Solutions.** Jnanendra Chandra Ghosh (T., 1918, **113**, 449—458).—The fact that the ionisation of strong electrolytes, as measured by the electrical conductivity or osmotic methods, does not vary with the dilution in accordance with the requirements of the law of mass action, is supposed to be due to the invalidity of the fundamental idea underlying the Arrhenius ionic theory. According to the author, strong electrolytes are completely ionised, and there is no question of an equilibrium between ions and unionised molecules. The relations between the ions are determined solely by the electrical forces acting between the ions, and the interior of a solution of a strong electrolyte is characterised by a certain potential, $A$, which affords a measure of the work which is required to remove the ions from the influence of their mutual attractive forces. By application of the kinetic theory, it may be inferred that ions become "free" when their velocity exceeds a certain critical value. The fraction of the free ions is equal to $e^{-A/nRT}$, in which $n$ is the number of ions formed from a molecule of the electrolyte. Denoting the Avogadro number by $N$, then the number of free ions is $nNe^{-A/nRT}$. At infinite dilution $A=0$, and the number of free ions $= nN$. From this follows $A = nRT \log_e \mu_\infty / \mu_v$ (1).

Assuming that the marshalling of the ions in solution corresponds with the arrangement of the atoms in the crystallised electrolyte, and that the component ions form a completely saturated electrical doublet, it is possible to calculate $A$ from the charge $E$ carried by the ions and $r$ their distance apart. In the case of a binary electrolyte, the equation is $A = E^2/Dr$, where $D$ is the dielectric constant of the solvent medium and $r = \sqrt[3]{v/2N}$ (2). From equations (1) and (2), the value of $\mu_v$ may be calculated for varying dilutions, and it is shown that the calculated values are in close agreement with those found by experiment between $v = 10$ and $v = 5000$. The agreement is also good in the case of ternary electrolytes. For bi-bivalent electrolytes, agreement is found for dilutions between $v = 10$ and $v = 100$, but at $v = 1000$ the observed conductivities are much greater than those calculated from the author's formula. The discrepancy is said to be due to hydrolysis.

On account of the diminution of the dielectric constant with rise of temperature, the value of $\mu_v/\mu_\infty$ should decrease. The observed diminution for potassium chloride at 100° is shown to be in satisfactory agreement with that calculated from the author's formula. H. M. D.

**"The Magnetic Properties of Zinc Blende and some other Minerals."** F. Stutzer, W. Gross and K. Bornemann (*Metall und Erz*, 1918, **15**, i, 1—9).—A method is described for measuring the magnetic susceptibility of paramagnetic minerals such as zinc blende, and a list of values of this constant given for fifty-three samples. F. C. T.

**Theoretical and Experimental Investigation of the Thermal Conductivity of Mixtures of Gases.** Sophus Weber (*Ann. Physik*, 1917, [iv], **54**, 481—502).—The theory of the thermal conductivity of gas mixtures is discussed in reference to the experimental data recorded in the literature. New measurements have been made for mixtures of hydrogen and carbon dioxide and of nitrogen and argon, and it is found that the results may be satisfactorily represented by the formula

$$K = K_1/(1 + A p_2/p_1) + K_2/(1 + B p_1/p_2),$$

in which $K_1$ and $K_2$ are the thermal conductivities of the constituent gases, $p_1$ and $p_2$ the partial pressures of the components in the mixture for which the conductivity is $K$, and $A$ and $B$ are empirical constants. These constants differ very widely from those which are indicated by theory. In the case of mixtures of hydrogen and carbon dioxide, the values of the constants indicated by theory are $A = 1{\cdot}01$ and $B = 2{\cdot}56$, whilst the empirical values which satisfy the experimental results are $A = 2{\cdot}70$ and $B = 0{\cdot}40$. For mixtures of nitrogen and argon, the empirical values are $A = 1{\cdot}07$ and $B = 0{\cdot}95$. Since the constants are in this case nearly equal, it follows that the thermal conductivity of mixtures is approximately given by the mixture formula, according to which $K = K_1 \cdot p_1/(p_1 + p_2) + K_2 \cdot p_2/(p_1 + p_2)$. H. M. D.

**Theory of Specific Heats.** Carl Drucker (*Zeitsch. Elektrochem.*, 1918, **24**, 83—84).—Polemical, in which the author criticises the method employed by Jankowsky (this vol., ii, 59) in deducing certain relationships for the specific heat of gases. The deductions drawn from the mathematical expressions are also criticised. J. F. S.

**Specific Heat at Low Temperatures. IV. Measurements of the Specific Heat of Liquid Hydrogen. Preliminary Results on the Specific Heat of Solid Hydrogen and on the Heat of Fusion of Hydrogen.** W. H. KEESOM and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1000—1004. Compare A., 1916, ii, 371).—The apparatus previously described has been used in the determination of the specific heat of liquid hydrogen. According to the most complete of several series of measurements, the atomic heat increases from 1·75 at 14·82° (abs.) to 2·26 at 20·11°.

The data obtained for solid hydrogen gave a mean value of 0·64 at 12·55° for the atomic heat, and for the latent heat of fusion the value 15 was obtained as the mean of two experiments. H. M. D.

**Specific Heats of Lead-Antimony Alloys.** R. DURRER (*Physikal. Zeitsch.*, 1918, **19**, 86—88).—Within the limits of experimental error, the specific heat of alloys of lead and antimony agrees with that calculated from the specific heats of the components by the simple mixture rule. The specific heat (between 0° and 100°) is actually represented by the equation

$$S = 0{\cdot}04965 - 0{\cdot}0001884\,p,$$

where $p$ is the percentage of lead in the alloy. The freezing-point diagram for this pair of metals shows that there are two curves meeting in a eutectic point at 249°. H. M. D.

**Atomic Heats of Tungsten and Carbon at Incandescent Temperatures.** A. G. WORTHING (*J. Franklin Inst.*, 1918, **185**, 707—708).—Many of the theories, based on the quantum hypothesis, for explaining the variation of the atomic heat with temperature, lead to the value 5·95 cal. per gram-atom degree as the upper limit for this quantity. With the object of testing these conclusions, the atomic heats of tungsten and carbon have been determined at high temperatures. The elements were used as filaments contained in closed globes at constant pressure; the heating was electrical, and the rate of cooling was determined by means of a potentiometer and a pendulum which operated switches at various points in its path. In the case of tungsten, the atomic heat is shown to vary almost lineally from 6·25 cal. per gram-atom degree at 1200° to 7·35 cal. per gram-atom degree at 2400°. That is, at these temperatures it has an atomic heat which is considerably above the theoretical maximum value, 5·95. In the case of carbon, the value varies from 5·35 at 1200° to 6·05 at 2000°. J. F. S.

**Melting Point Apparatus.** J. C. HIBBERT and W. F. THOMPSON (*Analyst*, 1918, **43**, 216).—A test-tube, 7 inches by 1·4 inches, is supported in a clamp and closed by a cork; the thermometer is attached to a glass tube passing through the cork. The stirrer also passes through a slot in the cork and is supported by rubber rings connected with a bent wire fixed to the clamp stand. The burner is provided with a glass wind-screen. W. P. S.

**Sulphur as a Cryoscopic Solvent.** E. Beckmann and C. Platzmann (*Zeitsch. anorg. Chem.*, 1918, **102**, 201—214).—In spite of the facility with which it undergoes transformation into allotropic modifications, sulphur can be successfully used as a cryoscopic solvent if certain conditions are fulfilled. Soon after having been melted, the freezing point of sulphur is about 119°, but after it has been kept for some hours at a temperature just above its melting point, the freezing point falls to 114·5°, and in this condition the sulphur is suitable for cryoscopic determinations. The apparatus and method employed have been previously described (A., 1897, ii, 88).

The cryoscopic constant of sulphur was determined by means of a number of organic compounds, bromoform (229·3), phenylthiocarbimide (226·6), naphthalene (211·4), diphenyl (208·4), thymol (206·4), quinoline (205·7), β-naphthol (205·2), and aniline (201·8), the mean value of $K$ being 213. The latent heat of fusion $w$, calculated from van't Hoff's equation, is 14·1 gram cal., a value somewhat higher than that determined experimentally for monoclinic sulphur. In accordance with its low dielectric coefficient, 4·0, sulphur shows no dissociating power. Substances of an acidic character like *p*-cresol and α-naphthoic acid show a tendency to associate to double molecules, the value of $K$ falling with increasing concentration.

The "natural" m. p. of sulphur, 114·5°, corresponds with a content of about 3·6% $S_\mu$. The observation of A. Smith (A., 1907, ii, 20), that the attainment of a steady m. p. by sulphur is delayed by sulphur dioxide and accelerated by ammonia, is confirmed. Organic compounds of a neutral or acidic character resemble the former, whilst basic substances, such as pyridine and aniline, resemble ammonia in their behaviour. These substances act catalytically by delaying or accelerating the formation of $S_\mu$, which may itself, however, be formed from $S_\pi$.

Arsenic trisulphide in sulphur has the simple molecule $As_2S_3$, but tends to polymerise with increasing concentration. Selenium tetrachloride shows a molecular weight of half the normal value, and this is attributed to the formation of selenium and sulphur monochlorides. E. H. R.

**Measurement of Low Temperatures. XXVII. Vapour Pressures of Hydrogen in the Neighbourhood of the Boiling Point and between the Boiling Point and the Critical Temperature.** P. G. Cath and H. Kamerlingh Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 991—999. Compare A., 1914, ii, 27).—An improved form of helium gas thermometer is described, and an account is given of the apparatus and methods employed in the further measurement of the vapour pressure of liquid hydrogen at temperatures ranging from the boiling point to the critical point. H. M. D.

**The Saturated Vapour Pressures of Tetratomic Substances.** E. ARIÈS (*Compt. rend.*, 1918, **166**, 802—805).—On the basis of the vapour pressures of ammonia given in the *Recueil de Constantes physiques*, the formula for the saturated vapour pressures of tetratomic substances is given as $\Pi = \tau^{17/6}Z/x$, where $x=[1+(1-\tau)(0{\cdot}84-\tau)/(\tau^2+1)]\tau^{11/6}$. Whilst the observed values for phosphorus trichloride are in fair agreement with those calculated from this formula, the agreement is not so good in the case of acetylene. W. G.

**The Association of Organic Compounds in Benzene and Alcohol Solution as determined by the Vapour Pressure Method.** WILLIAM ROSS INNES (T., 1918, **113**, 410—435).—The vapour pressures of benzene and ethyl alcohol when mixed with varying quantities of non-volatile substances have been measured at certain fixed temperatures. From the experimental data, the author has calculated the apparent molecular weight of the non-volatile substance by making use of the equation for Raoult's law. If $g$ grams of the substance of molecular weight $m$ are dissolved in $G$ grams of the volatile solvent of molecular weight $M$, and the vapour pressures of the pure solvent and solution are $p$ and $p'$, then this equation may be written in the form $m'=gMp'/G(p-p')$, where $m'$ is the apparent molecular weight of the non-volatile solute. The results obtained are shown by means of curves, in which $m'/m$ is plotted as a function of the percentage molecular concentration of the solute.

When benzene is used as solvent, the curves obtained may be divided into groups. In one of these, the substances have values of $m'/m$ which differ but little from unity even when the molecular concentration of the substance is very large. Acids and oximes form a group showing considerable association. In the case of formanilide and acetanilide, the value of $m'/m$ increases rapidly with the concentration, and a maximum appears to be reached. Ethyl tartrate is extremely abnormal in that very high values are found for $m'/m$, which reaches a maximum when the percentage molecular concentration is about 50 and diminishes rapidly at higher concentrations.

In alcohol as solvent, four substances were examined, and all gave values of $m'/m$ which increase with the concentration. In the case of azobenzene, which is readily soluble in hot alcohol, the association factor seems to increase continuously with the concentration. The value of $m'/m$ obtained for this substance in 60% solution is about 6·0.

The theoretical interpretation of the results is discussed in some detail, and in this connexion attention is directed to results obtained for mixtures of sulphuric acid and water (compare T., 1904, **85**, 1345), according to which the apparent molecular weight is very small and decreases rapidly with increasing concentration.

H. M. D.

**Heats of Dilution and their Variations with Temperature.** FRANK R. PRATT (*J. Franklin Inst.*, 1918, **185**, 663—695).—The heat of dilution of solutions of a large number of salts has been determined at a series of temperatures with the object of testing the validity of the expression $dl/d\theta = -dH/dm$, in which $l$ is the heat of dilution, $\theta$ the temperature, $m$ the mass of the solution, and $H$ the heat capacity of the system. The measurements were made by the method of constant flow, in which two streams, of solution and water respectively at the same temperature, were allowed to mix continuously in a Dewar vessel at constant temperature. Solutions of sodium chloride, potassium chloride, barium chloride, strontium chloride, ammonium chloride, sodium hydroxide, potassium hydroxide, sodium nitrate, potassium nitrate, barium nitrate, strontium nitrate, and ammonium nitrate were used. The results indicate that in a general way the above formula is true. The discrepancies are discussed. A further series of measurements was made with the following non-electrolytes: resorcinol, dextrose, sucrose, catechol, quinol, mannose, and ethyl alcohol. The chief point of interest arising from these experiments is that for non-electrolytes $H$ is constant for all concentrations; on the whole, the results here are in general agreement with the above formula.

J. F. S.

**Possibility of Calculating the Properties of Liquids and Vapours.** JOHANNES GEISSLER (*Zeitsch. Elektrochem.*, 1918, **24**, 101—113).—A theoretical paper in which the author has shown that for the four substances fluorobenzene, benzene, ethyl ether, and carbon tetrachloride there is a region in which the physical properties can be represented by straight lines, and that within the limits of this area the physical properties can be calculated. Methods are worked out for calculating (1) the molecular volume of the saturated vapour from that of the liquid, (2) the molecular volume of a liquid from the temperature, (3) the coefficient of expansion of a liquid from the temperature, (4) the vapour pressure of a liquid from the temperature, (5) the change of vapour pressure per degree at a given temperature, (6) the latent heat of vaporisation of a liquid at a given temperature. The calculated and experimental values are compared, and it is shown that whilst there is good agreement in many cases, there are also divergences. The latter are attributed to the use of data obtained in a region removed from the limited region mentioned above, or from data in the neighbourhood of the freezing point.

J. F. S.

**Atomic and Molecular Numbers.** HERBERT STANLEY ALLEN (T., 1918, **113**, 389—396).—A short account is given of the significance of the atomic number in connexion with the periodic classification of the elements. The atomic numbers of analogous elements differ by eight or a multiple of eight, or in some cases by a number which is two units greater than one of the foregoing. The reason for these variations from the rule of eight is the presence of three elements in group VIII of the periodic table.

Molecular numbers of analogous compounds show similar relations. In reference to organic compounds, it is pointed out that the molecular number for the group $\cdot CH_2\cdot$ is eight, and the rule of eight is consequently of wide application in organic chemistry. It is probable that many properties of chemical compounds will be found to depend on the values of the molecular numbers.

H. M. D.

**Modified Mercurial Viscosimeter for Determining the Viscosity of Volatile Liquids.** F. M. Lidstone (*J. Soc. Chem. Ind.*, 1918, **37**, 148—149T).—In the apparatus described, an attachment is provided by means of which an equal excess pressure may be applied above and below the moving column of liquid in the viscometer. This prevents the formation of a cushion of vapour between the mercury and the volatile liquid under examination, but does not interfere with the usual constants of the instrument.

W. P S.

**The Viscosity of Liquefied Gases. X. The Viscosity of Liquid Hydrogen.** J. E. Verschaffelt (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 986—990. Compare A., 1917, ii, 408).—From observations on the time of oscillation of a specially designed oscillatory system immersed in the liquid hydrogen, the viscosity at 20·4° (abs.) has been found to be $\eta = 0{\cdot}000130$, with an estimated accuracy of about 1%. A preliminary determination of the viscosity of the saturated vapour at this temperature (vapour pressure = 76·9 cm.) gave $\eta = 0{\cdot}000010$.

H. M. D.

**Solubility Measurements.** Stewart J. Lloyd (*J. Physical Chem.*, 1918, **22**, 300—302).—The measurements recorded were made incidentally in connexion with other work. The solubility of sulphur dioxide in benzene, toluene, nitrobenzene, *o*-nitrotoluene, and acetic anhydride was measured at various temperatures. At 20°, the solutions saturated at 756—760 mm. contain the following amounts in grams per litre: toluene, 236·0; nitrobenzene, 267·4; *o*-nitrotoluene, 236·0; acetic anhydride, 106. The solubility of aluminium chloride in carbon tetrachloride decreases from 0·74 at 4° to 0·06 gram per litre at 34°; in chloroform, from 1·00 at 0° to 0·72 at 25° and 0·65 at −15°. The solubility of barium chloride in nitrobenzene increases from 0·167 at 20° to 0·40 at 100°, and that of benzoic acid in ethyl acetate from 8·0 grams per litre at −6·5° to 37·7 at 21·5° and 95·7 at 75°.

H. M. D.

**Reactions between Solid Substances.** Leslie Henry Parker (T., 1918, **113**, 396—409. Compare T., 1914, **105**, 1504). —The rate at which certain solid substances react together has been examined systematically by observations at various temperatures up to and above the fusion temperature. The pairs of substances investigated were sodium carbonate and barium sulphate, silver nitrate and sodium carbonate, cuprous chloride and sodium carbonate. In all cases, the mixtures were made from carefully dried substances. Although the results obtained show clearly that reaction takes place below the fusion temperature, and that the rate of the reaction between the solids increases continuously with rise of temperature, there is in all cases a very marked increase in the velocity at the temperature of fusion. The ratio of the velocity in the fused mixture to that at the highest temperature in the solid state varies in the three cases examined. It is immeasurably large in the mixture containing barium sulphate, is equal to about 150 for the mixture containing silver nitrate, and to about 20 for the mixture containing cuprous chloride.

The results seem to show that the liquid state per se has an influence on the rate of interaction, which influence is to be distinguished from that of temperature. The fact that shearing stresses give rise to reactions between solid substances does not seem as yet to be completely explained, and it is suggested that such stresses produce changes of state in the surface layers which are equivalent to that produced by fusion. H. M. D.

**Xanthic Acids and the Kinetics of their Decomposition. I.** Hans von Halban and Walter Hecht (*Zeitsch. Elektrochem.*, 1918, **24**, 65—82. Compare A., 1913, ii, 312).—The rate of decomposition of xanthic acid [ethyl hydrogen dithiocarbonate, $OEt\cdot CS\cdot SH$] and methyl hydrogen dithiocarbonate in water at 0° has been studied. The solubility of these substances in water was first determined, and found to be at 0°: xanthic acid, 0·02 mol. per litre; methyl hydrogen dithiocarbonate, 0·05 mol. per litre. The rate of decomposition was determined by dissolving a known amount of the sodium salt of the acid in question in water, and, when the solution had reached 0°, liberating the acid with a slight excess of hydrochloric acid, then after a measured interval of time neutralising with a cooled solution of sodium hydrogen carbonate and titrating with a 0·02*N*-iodine solution. It is shown that, contrary to the behaviour of solutions in organic solvents, the velocity constants in the present case, when calculated on the basis of a unimolecular reaction, decrease rapidly with decreasing concentration; the decomposition is positively catalysed by hydrogen ions. This leads to the assumption that both the undissociated molecules and the ions take part in the reaction. On the basis of this assumption, the dissociation constants of the acids were calculated, and found to be independent of the dilution, a fact which confirms the assumption. At 0°, the dissociation constant for methyl hydrogen dithiocarbonate is found to be 0·034, and that for xanthic acid 0·030. The addition of sulphates (Na, Mg, $NH_4$) to the decomposing xanthic acids in water solution strongly retards the action; for example, 0·25*N*-magnesium sulphate reduces the velocity of decomposition to one-third of the original value, and 3*N*-ammonium sulphate reduces it to one-sixth. A few velocity measurements have been made in ethyl alcohol, methyl alcohol, propyl alcohol, amyl alcohol, and benzyl alcohol solutions to complete the data published in an earlier paper (*loc. cit.*). Measurements were made at 0° on the partition of xanthic acid between water and carbon disulphide, chloroform, nitrobenzene, light petroleum, benzyl alcohol, and amyl alcohol respectively. It is shown that the dependence of the partition coefficient on the dilution is in accord with the dissociation constant calculated from the velocity values. The absorption spectrum of solutions of xanthic acid in light petroleum, $0{\cdot}5N$-ethyl alcohol in light petroleum, and in diethyl ether was measured, but although the rate of decomposition is very different in the different solvents, no difference could be observed in the absorption curves. Benzyl hydrogen dithiocarbonate was prepared from the potassium salt. This substance is a solid, m. p. 29°, and when quite pure may be kept for several hours, and in non-hydroxy-solvents has a normal molecular weight. The solubility and rate of decomposition have been determined in twelve solvents. The saturated solution at 0° has the following concentration in these solvents: hexane $0{\cdot}224N$, light petroleum $0{\cdot}316N$, methyl alcohol $0{\cdot}36N$, acetic acid $0{\cdot}41N$, nitromethane $1{\cdot}49N$, acetonitrile $3{\cdot}26N$, carbon disulphide $3{\cdot}70N$, acetone $3{\cdot}41N$, diethyl ether $2{\cdot}93N$, benzene $3{\cdot}33N$, ethyl bromide $3{\cdot}88N$, and nitrobenzene $3{\cdot}15N$. The van't Hoff velocity constant was calculated from the data, and these values, as well as those for xanthic acid, show that the catalytic influence of the solvent is not removed by the van't Hoff calculation. J. F. S.

**Hydrolysis of Ethyl Citrate and the Ethyl Hydrogen Citrates.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1918, **24**, 84—85).—Polemical; the author claims that the work of Pinnow (this vol., ii, 103) is not the first case in which the hydrolysis of a tribasic ester has been studied, and then proceeds to criticise the results published by Pinnow. J. F. S.

**The Influence of Lipoids on the Rate of Reaction.** M. SIEGFRIED (*Biochem. Zeitsch.*, 1918, **86**, 98—109).—Lecithin inhibits the transformation of the yellow mercuric iodide into the red variety, and also the reduction of ammoniacal silver nitrate by phenylhydrazine. The latter reaction should be carried out in the dark, and in the presence even of diffuse sunlight the inhibiting action of the lipoid is diminished. S. B. S.

**Ester Catalysis of γ-Lactones.** HJALMAR JOHANSSON and HUGO SEBELIUS (*Ber.*, 1918, **51**, 480—485).—It has recently been shown that the hydrolysis of β-lactones to the hydroxy-acids is not catalysed by hydrogen ions (*Lunds universitets årsskrift*, 1916), and it appeared to be of interest, therefore, to determine directly whether the hydrolysis of γ-lactones, like the formation of them (compare Taylor and Close, A., 1917, ii, 253), is catalysed by acids.

For this purpose, the catalysis of the hydrolysis of γ-valerolactone and γ-butyrolactone by nitric acid has been studied, the hydroxy-acid being titrated by means of barium hydroxide. It is found that in the case of γ-butyrolactone, with quantities of nitric acid represented by 9, 3, and 1, the time required for the production of the same percentage of hydroxy-acid is represented very nearly by 1, 3, and 9. The results with valerolactone are similar; H-ion concentration, 6:3:1 (roughly), and times, 1:3:6. The hydrolysis of γ-lactones is therefore a normal case of ester catalysis.

J. C. W.

**Errors affecting Determinations of Atomic Weight. VII. Refinements in the Method of Weighing: Microbalance: Application to the Atomic Weight of Helium and Hydrogen.** PH. A. GUYE (*J. Chim. Phys.*, 1918, **16**, 46—61. Compare A., 1916, ii, 385, 386, 432, 435; this vol., ii, 40, 41).—The Taylor microbalance is discussed by the author and shown to be very suitable for the accurate determination of gaseous densities. Correct formulæ are developed for calculation of the density and molecular weight of gases from the experimental figures obtained in this way. These formulæ have been applied to the experimental figures obtained by Taylor (*Phys. Review*, 1917, **10**, 653), when the following values were obtained: normal litre of hydrogen weighs 0·089858 gram, molecular weight 2·0151; normal litre of helium weighs 0·17835 gram, molecular weight 3·9976. These values differ by about 10 per 10,000 from those calculated by Taylor. It is further shown that the Taylor microbalance appears to be susceptible of a few improvements, which are indicated by the author, and which, being made, give an instrument which will not only give the densities and molecular weights of gases with a precision at least equal to that of other methods, but which, with very small quantities of material, will give all the weighings necessary for the determination of atomic ratios. The great interest of the method lies in the fact that the determination of mass will resolve itself into the measurement of length, which is much more precise than weighing with weights, no matter how carefully calibrated.

J. F. S.

**The Conception of the Chemical Element and the Phenomenon of Isotopy (Addendum).** K. FAJANS (*Jahr. Radioaktiv. Elektronik*, 1918, **15**, 101—102. Compare A., 1917, ii, 566).—In further pressing the point of view that isotopic elements cannot be considered as one element, in Boyle's sense of undecomposability, an intimate mechanical mixture of isotopes is postulated as capable of being made and of existing as such in nature, which, since they can be imagined to be capable of being resolved into their constituents, if of different density, by the use of suitable fluids, cannot be regarded as undecomposable.

F. S.

**Molecular Frequency and Molecular Number. III. Inorganic Compounds. Lindemann's Formula.** H. Stanley Allen (*Phil. Mag.*, 1918, [vi], **35**, 445—460. Compare this vol., ii, 163).—According to Lindemann, the characteristic molecular frequency of a compound is given by the formula $\nu = k\sqrt{T_s/MV^{\frac{2}{3}}}$. in which $M$ is the molecular weight, $V$ the molecular volume, and $T_s$ the melting point of the compound on the absolute scale. Assuming $k = 3{\cdot}08 \times 10^{12}$, this formula has been used to calculate the frequency for a large number of inorganic compounds. The results, which are arranged according to the periodic groups, afford further evidence of the validity of the relation $N\nu = n\nu_A$ or $N\nu = (n + \frac{1}{2})\nu_A$, according to which the product of the molecular number and the characteristic frequency is a simple multiple of the fundamental frequency $\nu_A$.

The fact that this relation holds for compounds which include elements belonging to all the different groups of the periodic system makes it appear very probable that the above equation is the expression of a relation which is of fundamental importance and characteristic of the solid state of matter. H. M. D.

**Periodic System of the Elements.** Charles P. Steinmetz (*J. Amer. Chem. Soc.*, 1918, **40**, 733—739).—It is shown that the single, double, and quadruple periodicities which characterise the periodic system can be completely represented by a Riemann surface having two singular points at −40 and −130. Incidentally, it is pointed out that it is unjustifiable to assume that the functional relation between the properties of the elements and their atomic weights can be represented on a plane. H. M. D.

**The Ductility of Metals and their Position in the Periodic System.** G. Tammann (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 247—254; from *Chem. Zentr.*, 1918, i, 509—510).—Lothar Meyer indicated that the ductile elements lie near the maxima and minima of the atomic volume curve. The author regards the occurrence of ductility as dependent on the formation of as many slip-planes as possible in the direction of main extension and the occurrence of movement with as little force as possible, and he uses the term ductility in the commonly accepted sense of capacity to be drawn into wire. Pairs of elements which form a continuous series of mixed crystals are regarded as isomorphous, so that by starting from a known crystal lattice it is possible to find many other examples of the same type. In the periodic system, a certain symmetry prevails in the crystalline form of the typical crystals, but is interrupted by the non-metallic elements of the carbon group. Elements with various crystalline forms are ductile. The ductility is not dependent on any definite space lattice, but probably on the occurrence of only one kind of atoms, between which no valencies are active, in the lattice of their crystals. If the valencies between the atoms of the lattice become active, as in the binary compounds of the metals, the formation of slip-bands is checked and the ductility disappears. D. F. T.

**The Relationship of the Rare Earths to the Periodic System.** RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1918, **102**, 177—200).—The many attempts which have been made to fit the elements of the rare earths into existing groups of the periodic classification have all been unsatisfactory. There is only slight chemical and crystallographic justification for placing lanthanum in the third and cerium in the fourth group, and in any case the valency of an element or the isomorphism displayed by certain of its salts serves as a very uncertain guide to its true relationship to other elements. The author agrees with Tammann that an element should show little or no chemical affinity for another element belonging to the same group; conversely, if two elements form a stable compound, they cannot belong to the same group. When this test is applied to the only rare earth element which is available in sufficient quantity for systematic study, cerium, it must be concluded that this element can belong to none of the ordinary groups of the periodic system. It forms binary compounds with metals of every group, with the exception of those of groups VI and VII, which have not been studied, and many of these compounds are remarkable for their great heats of formation and high melting points. In particular, cerium combines energetically with elements of groups III, IV, and V to form such compounds as $CeAl_2$ (m. p. 1460°), $CeAl_4$ (m. p. 1250°), $Ce_2Sn$ (m. p. 1400°), and $Ce_4Bi_3$ (m. p. 1630°), whilst lanthanum also forms with aluminium a strongly exothermic compound, $LaAl_4$, of high melting point.

The new periodic law, based on the atomic numbers of the elements, requires the existence of sixteen elements between Ba(56) and Ta(73). Of these, fourteen rare earth elements are known, one being missing between Nd and Sm, and one between Lu and Ta. Whilst, therefore, the sixteen rare earth elements must form a continuous series with the remaining elements, they must form a special group by themselves.

A satisfactory representation of the position of the rare earth group in the family of elements is obtained in the following manner. The elements are arranged in order of atomic numbers on an ascending spiral, each turn of which corresponds with one short period of eight elements, elements belonging to the same group appearing vertically above one another. After passing Ba, the spiral changes its course and develops a subsidiary, smaller loop which, after making rather more than a complete turn, rejoins the original path of the spiral at Ta, group V. On this subsidiary loop are crowded the sixteen rare earth elements, which form a closely related family independent of the other groups situated on the main spiral. The elements La and Ce appear on the small loop in fairly close proximity to the vertical lines through groups III and IV respectively on the principal spiral, and this may account for certain properties shown by La and Ce in common with the elements of groups III and IV respectively. The rare earth elements themselves exhibit a certain periodicity in their basicity, magnetic properties, and in the solubility of their salts;

such periodicity or gradual change of properties is to be inferred from the form of the loop.

It is further suggested that the triads Fe,Co,Ni, Ru,Rh,Pd, Os,Ir,Pt also form three secondary loops on the principal spiral in place of elements belonging to group VIII. Each triad then forms a sub-group similar in character to the rare earth group, and homologous elements of the three triads appear on vertical lines parallel to the axis of the spiral. It is significant that the typical magnetic elements Fe, Co, Ni, and also the strongly paramagnetic elements Tb, Dy, and Ho, are all among those elements which do not conform to the normal course of the periodic system. E. H. R.

**Gas Generating Apparatus.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 64).—An apparatus for generating small quantities of hydrogen sulphide, carbon dioxide, hydrogen, etc., consists of a wide tube constricted at its middle so as to form two short, cylindrical bulbs; the upper bulb is provided with a tap and contains the ferrous sulphide or calcium carbonate, etc., whilst the lower bulb is connected by a glass tube to an acid reservoir at some height above the bulbs. The whole apparatus is made in one piece. W. P. S.

**Experimental Retort for Dry Distillation.** F. E. COOMBS (*Met. and Chem. Eng.*, 1918, **18**, 425).—The retort consists of a cylinder of metal closed at the bottom. A similar cylinder, but of slightly larger diameter, so as to slide loosely over the retort, forms the lid, to which a bent delivery tube is fitted. The lid is secured to the retort by screws. The apparatus is placed in a bath of fused metal or sodium hydroxide, the level of which is below the top of the retort, which is now sealed by the liquid entering the annular space inside the lid. The contents of the retort can be distilled at a known and regulated temperature. The advantage claimed is accessibility for cleaning and charging. H. J. H.

**Extraction Apparatus for the Laboratory.** CARL G. SCHWALBE and WALTER SCHULZ (*Chem. Zeit.*, 1918, **42**, 194).—A modification of the Besson extractor (A., 1916, ii, 26) in which no corks are employed and larger quantities (4—6 litres) of material may be extracted. The apparatus consists of a white metal cylinder in the upper part of which is fitted a wire ring which carries a fine cotton bag holding the material to be extracted. Above this bag is fitted a cylindrical condenser, through which a stream of water flows. The apparatus stands in a water-bath heated by a gas burner in the usual manner. All gas- and water-connexions are made of metal so as to ensure the safety of the apparatus. A. B. S.

**Simple Arrangement for Simultaneous Stirring and Filtration.** FRITZ FEIGL (*Zeitsch. angew. Chem.*, 1918, **31**, i, 68).—To obviate the errors which occur when portions of a saturated solution at high temperatures are removed for solubility determinations, the author describes a combined stirrer and filter. The apparatus consists of a stout-walled, wide test-tube from which the bottom has been removed, and on to the sides of which a number of glass vanes have been fastened. One end of the tube is covered with a piece of linen or hardened filter paper, the other end is inserted into a hole in a wooden pulley. The tube is then partly immersed in the saturated solution and rotated; the clear, saturated solution slowly filters into the tube, whence it can be withdrawn in suitable quantities. If a semipermeable membrane is substituted for the filter paper, the apparatus may be used to determine the velocity of diffusion of colloids below their coagulation temperature.

J. F. S.

**Grinding Glass Tips for Drop-weight Apparatus.** EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1918, **40**, 784—785).—For the measurement of surface tension by the drop weight method, it is necessary to prepare capillary tips of circular cross-section by grinding until the section is flat and smooth and the edges are perfectly sharp. To facilitate this, the author recommends the use of Wood's metal or other similar low melting alloy. The glass tube, made ready for the final adjustment of the tip, is lowered into the molten alloy, some of which is drawn into the capillary. The tube is left in position until the alloy has solidified, when the tip becomes firmly embedded in the alloy. The tube and alloy are then ground until the requisite sharp edge is obtained.

H. M. D.

**Willem Homberg.** F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 602—605).—Further particulars of the life of the alchemist Homberg, including a reproduction of part of an autograph letter (compare this vol., A., ii, 164). A. J. W.

**Anselmus Boëtius de Boodt.** F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 628—671).—An account of the life and researches of the mineralogist de Boodt, who was born at Bruges in 1550, and died at the same place on June 21st, 1632.

A. J. W.

**Lecture Experiments for Demonstrating the Law of Multiple Proportions.** F. EMICH (*Zeitsch. anal. Chem.*, 1918, **57**, 65—71).—Simple experiments are described, and comprise the estimation of oxygen in cupric and cuprous oxides by reduction with hydrogen, the formation of normal potassium tartrate and potassium hydrogen tartrate, and the gasometric estimation of carbon dioxide in sodium carbonate and sodium hydrogen carbonate. W. P. S.

**Some Lecture Experiments with Silver Carbide. [Acetylide].** JOHN EGGERT and HANS SCHIMANK (*Ber.*, 1918, **51**, 454—456. Compare A., 1917, ii, 462).—The experiments are designed to show that pure silver carbide detonates very mildly in a vacuum, its bursting power under ordinary conditions being due to the rapid heating and expansion of the surrounding air.

J. C. W.

# Inorganic Chemistry.

**The Relation of Iodine to Sulphur and Selenium.** E. BECKMANN and C. PLATZMANN (*Zeitsch. anorg. Chem.*, 1918, **102**, 215—222).—The molecular weight of iodine determined cryoscopically in sulphur (K = 213) corresponds with $I_2$. Sulphur dissolved in iodine has the molecular composition $S_8$, but in the same solvent, selenium is dissociated into $Se_2$ and $Se_1$, although in organic solvents it exists as $Se_8$, and iodine, on account of its low dielectric constant, would not be expected to have dissociating properties. The freezing point of sulphur is raised by selenium, as is to be expected, since the two substances are isomorphous. On account of the sparing solubility of selenium in sulphur, experimental determinations were limited to concentrations up to 2·5% Se. Over this range, the elevation of the freezing point was approximately proportional to the concentration, and averaged 0·242° per 1% Se. It is concluded that in sulphur–selenium mixtures the latter is present as $Se_8$.

The depression of the freezing point of sulphur–selenium mixtures by iodine and diphenyl was determined. The cryoscopic constants of mixtures containing up to 1·58% Se were found to be practically equal to that of sulphur alone. On the assumption that the change of the freezing point of sulphur containing selenium and iodine is the algebraic sum of the elevation due to $Se_8$ and the depression due to $I_2$, the total effect was calculated and the result compared with the observed value for a number of concentrations. The agreement was generally satisfactory. There is no evidence of the formation of a compound between selenium and iodine, and the low molecular weight of selenium in iodine solution remains unexplained. E. H. R.

**Action of Thionyl and Sulphuryl Chlorides on Sulphur and Phosphorus.** H. B. NORTH and J. CLAUDE THOMSON (*J. Amer. Chem. Soc.*, 1918, **40**, 774—777).—Thionyl and sulphuryl chlorides were heated in sealed glass tubes with sulphur and phosphorus at temperatures ranging from 70° to 180°. Both chlorides react with sulphur at 150° to 180°, with the formation of sulphur dioxide and sulphur monochloride. Under similar conditions, the two chlorides react with both red and yellow phosphorus, with the formation of phosphorus trichloride, according to the equations $3SO_2Cl_2 + 2P = 2PCl_3 + 3SO_2$, $4SOCl_2 + 2P = 2PCl_3 + 2SO_2 + S_2Cl_2$. Prolonged heating tends to produce phosphorus pentachloride in accordance with the equations $PCl_3 + SO_2Cl_2 = PCl_5 + SO_2$, $3PCl_3 + 4SOCl_2 = 3PCl_5 + 2SO_2 + S_2Cl_2$, but these reactions are far from complete after heating for several hours at 160—180° in presence of considerable excess of the sulphuryl or thionyl chloride. H. M. D.

**Oxidation of Sulphur Dioxide and Ammonia in the Presence of Platinum and Rhodium.** P. WENGER and C. URFER (*Ann. Chim. anal.*, 1918, **23**, 97—104).—Maximum oxidation of sulphur dioxide takes place at 432° in the presence of platinum black, 96·8% of the dioxide being converted into sulphur trioxide. When rhodium black is used as the catalyst, the maximum oxidation (91·1%) occurs at 610°. In the case of ammonia, 97% is converted into nitric and nitrous acids by platinum black at 533° to 562°, whilst with rhodium black a maximum oxidation of 69·7% is attained at 662°. W. P. S.

**Synthesis of Ammonia at High Temperatures. II.** EDWARD BRADFORD MAXTED (T., 1918, **113**, 386—389. Compare *ibid.*, 168).—Further observations on the combination of nitrogen and hydrogen at high temperatures have been made by passing the 1:3 mixture through a capillary tube fitted with platinum wire electrodes, between which sparks were made to pass by connecting the wires with an induction coil. When the distance between the electrodes is gradually reduced, the ordinary spark discharge is transformed into a small high-tension arc characterised by a continuous flame of high temperature. In experiments in which the rate of passage of the gas was kept constant and the size of the gap reduced, it was found that this was accompanied by a continuous increase in the percentage of ammonia formed. Similar results were obtained when the speed of the gas was controlled so as to give a constant time of contact. For a fixed width of gap, the percentage of ammonia was found to increase as the rate of flow of the gaseous mixture diminished. The results generally are in agreement with those obtained in the previous high-temperature measurements (*loc. cit.*). H. M. D.

**Synthesis of Nitrosyl Bromide.** E. MOLES (*J. Chim. Phys.*, 1918, **16**, 3—10; *Anal. Fis. Quim.*, 1918, **16**, 377—385).—The author has examined the reaction of nitric oxide on bromine, and the nature of the resulting nitrosyl bromide, with the object of ascertaining whether this substance is suitable for use in the determination of the atomic weight of bromine by the method employed by Wourtzel (A., 1913, ii, 771) for chlorine with nitrosyl chloride. After a series of very careful experiments, it is found that the nitrosyl bromide produced always contains a slight excess of bromine, and consequently the compound is of no use for the purpose of determining atomic weights. J. F. S.

**Preparation of Carbon Tetrachloride from Carbon Disulphide and Chlorine.** ISCO CHEMICAL CO. (U.S. Pats. 1260621 and 1260622).—Carbon disulphide containing free sulphur is treated with chlorine in the presence of a catalyst to form sulphur dichloride and carbon tetrachloride, and an additional quantity of carbon disulphide is then added to convert the sulphur dichloride into sulphur monochloride, with the formation of more carbon tetrachloride. The product is treated with sufficient tin to convert the sulphur monochloride into sulphur, with the formation of stannic chloride, and, after separating the sulphur, water is added to hydrate the stannic chloride, and the carbon tetrachloride is recovered from the mixture by distillation. A. S.

**Causticising of Potassium Carbonate.** E. BELLONI (*Ann. Chim. Applicata*, 1918, **9**, 115—149).—The reaction between potassium carbonate and calcium hydroxide is reversible, and may be represented as a heterogeneous system in which there are two solid phases and one liquid phase containing variable proportions of the other components. From mathematical data based on the consideration of the formulæ of Bodländer and Lucas (A., 1905, ii, 634) and Le Blanc and Novotny (A., 1907, ii, 22), the following general isotherm for the conversion of an alkali carbonate into hydroxide by the action of calcium hydroxide has been deduced: $C^2{}_{KOH(NaOH)}C/{}_{K_2CO_3(Na_2CO_3)} = a - a'\phi + a''\phi^2$, where $C^2{}_{KOH}$ represents the concentration in gram-molecules of alkali hydroxide, $C_{K_2CO_3}$ the concentration of the alkali carbonate in the final solution, and $\phi$ the concentration of the carbonate in the initial solution. The constant $K$, which represents any given concentration giving stable equilibrium, is a definite function of $\phi$ to which the form may be given $K = a - a'\phi + a''\phi^2$. In the special case of the conversion of potassium carbonate into hydroxide at 100°, and for values of $\phi$ varying from 0 to 1·5 (that is, for solutions up to $3N$), the equation assumes the form $C^2{}_{KOH} / C_{K_2CO_3} = 133{\cdot}20 - 127{\cdot}85\phi + 43{\cdot}50\phi^2$. The yield of potassium hydroxide obtainable from a solution of potassium carbonate of known concentration may be calculated by means of the equation $C_{KOH} = K(-0{\cdot}25 + \sqrt{0{\cdot}0625 + \phi/K})$. At equal molecular concentration of the solutions and under the same conditions of temperature, a greater yield of hydroxide is obtained from sodium carbonate than from potassium carbonate. The formation of a double carbonate of potassium and calcium at a given temperature is only possible at a single definite concentration, which at 100°, the temperature for technical preparation of hydroxide, is 61·78 grams per 100 c.c. This corresponds with a concentration much higher than is used in the manufacturing process. The temperature has a great influence on the velocity of the reaction, but does not affect the final stage of equilibrium. The results for equal concentrations, $\phi$, at 80° and 100° were practically identical. [See also *J. Soc. Chem. Ind.*, 368A.] C. A. M.

**Equilibria in Solutions containing Mixtures of Salts. I. The System Water and the Sulphates and Chlorides of Sodium and Potassium.** W. C. BLASDALE (*J. Ind. Eng. Chem.*, 1918, **10**, 344—347).—The conditions which govern the separation by fractional crystallisation of sodium and potassium salts were investigated by the aid of the phase rule diagrams for such solutions. The equilibrium conditions of the reversible reaction $3KCl + 2Na_2SO_4,10H_2O \rightleftarrows K_3Na(SO_4)_2 + 3NaCl + 20H_2O$ were studied, and the compositions of the solutions saturated with one or more of these salts at 0°, 25°, 50°, 75°, and 100° were determined and plotted with respect to four axes representing sodium sulphate, potassium sulphate, potassium chloride, and sodium chloride. The diagrams represent the composition of all possible solutions which can be in equilibrium with these four salts, and with Glauber's salt and sodium potassium sulphate (glaserite), and indicate the stability of glaserite under widely varying conditions. [For details, see *J. Soc. Chem. Ind.*, 369A.]

W. F. F.

**Separation of Sodium and Potassium Chlorides and Sulphates by Fractional Crystallisation.** W. C. Blasdale (*J. Ind. Eng. Chem.*, 1918, **10**, 347—353).—The application of the principles described in the preceding abstract to the separation of mixed solutions is shown. Diagrams are given representing the composition of mixed solutions of (1) potassium chloride and sodium chloride, (2) potassium chloride and potassium sulphate, (3) potassium sulphate and sodium sulphate, (4) sodium sulphate and sodium chloride, and (5) mixtures of potassium salts with sulphates and chlorides of sodium and potassium. The diagrams are used to determine possible cycles of operation by which the various salts may be successively crystallised by evaporating and cooling at suitable temperatures. [For details, see *J. Soc. Chem. Ind.*, 369A.]

W. F. F.

**Production of a Stable Sodium Percarbonate.** Henkel & Co. (D.R.-P., 303556, 1915; from *Chem. Zentr.*, 1918, i, 497).—A compound, $2Na_2CO_3,3H_2O_2$, is obtained by the addition of sodium carbonate to an aqueous solution containing at least a sesquimolecular proportion of hydrogen peroxide; instead of sodium carbonate and hydrogen peroxide being taken as such, these substances may be produced in the solution by a suitable chemical change, for example, from sodium peroxide and sodium hydrogen carbonate.

D. F. T.

**The Calcium Arsenates.** R. H. Robinson (*J. Agric. Res.*, 1918, **13**, 281—294).—Pure calcium hydrogen arsenate was prepared by pouring a calcium chloride solution slightly acidified with acetic, hydrochloric, or nitric acid into a sodium·hydrogen arsenate solution similarly acidified. A heavy, voluminous precipitate was formed, which was washed by decantation, filtered, washed with hot water until free from chlorides, and dried at 100°. The washings were evaporated to a small volume, when crystals separated, and were washed and dried. Analysis showed both the powder and crystals to have the formula $CaHAsO_4,H_2O$. The water of crystallisation was lost at 175°.

Pure tricalcium arsenate was prepared by pouring an alkaline calcium chloride solution into an alkaline sodium hydrogen arsenate solution. A heavy, voluminous precipitate was formed, which was washed by centrifuging and decantation, and then filtered and dried at 100°. Analysis agreed with the formula $Ca_3(AsO_4)_2,2H_2O$. The water of crystallisation was lost at 175°.

The specific gravity of the salts was determined by weighing in specially dehydrated absolute alcohol at 20°. The results were: for $CaHAsO_4,H_2O$, $D_4^{20}$ 3·09; for $CaHAsO_4$, 3·48; for $Ca_3(AsO_4)_2,2H_2O$, 3·23; for $Ca_3(AsO_4)_2$, 3·31. Solubility was determined at 25° in a water-bath fitted with a revolving bottle-holder. One hundred grams of the solution contained in the case of $CaHAsO_4$ 0·3108 gram of the salt, and in the case of $Ca_3(AsO_4)_2$ 0·0133 gram.

J. H. J.

**An Artificial Patina.** OTTO GROTIAN (*Zeitsch. Elektrochem.*, 1918, **24**, 83).—The author describes a method of artificially producing an incrustation or patina on copper articles similar to that found on ancient bronzes. This film is produced by electrolysing a solution of copper sulphate between copper electrodes for three minutes with a current density of 1 amp./per sq. decimetre; the current is then interrupted and the cathode removed from the liquid. The anode is allowed to remain undisturbed in the liquid for twenty-four hours. The process is repeated several times, alternately passing the current for three minutes and leaving the anode for twenty-four hours. After several repetitions, the anode is removed and found to be covered with a beautiful bluish-green, non-crystalline patina, which cannot be removed by washing. On analysis, the film is shown to have the composition $CuO,3H_2O$.

J. F. S.

**Mercury Fulminate and its Estimation.** G. S. HEAVEN (*J. Soc. Chem. Ind.*, 1918, **37**, 143—147T).—Commercial mercury fulminate consists of a crystalline powder varying in colour from pale cream to dark brown; the largest crystals do not exceed 1 mm. in length, and these are more sensitive to impact than are the smaller crystals. A very fine powder, sifted through calico, fails to fire. Fulminate is soluble in alcohol, ammonia, pyridine, potassium cyanide solution, and in cold water, but is decomposed by hot water, alkali solutions, and thiosulphate solution. It does not inhibit the growth of fungi; *Tricoderma viride* and *Acrostalagmus albus Preuss* grow readily on bags containing fulminate, and even on the crystals themselves. The following method is recommended for the analysis of detonator composition containing fulminate, antimony sulphide, potassium chlorate, etc. A quantity of 0·3 gram of the sample is treated with 50 c.c. of *N*/10-thiosulphate solution, 0·3 gram of boric acid is added, the mixture is stirred for three minutes, and then titrated with sulphuric acid, using methyl-orange as indicator. The sulphuric acid is standardised previously against pure mercury fulminate. Any antimony sulphide which may be present is then collected on a filter, washed, dried, and weighed, or estimated volumetrically if the sample contains powdered glass. To the filtrate are added 100 c.c. of 10% ferrous sulphate solution containing 1 c.c. of free sulphuric acid, the mixture is boiled for thirty minutes, the mercury sulphide collected, dissolved in aqua regia, the solution neutralised with ammonia, acidified with hydrochloric acid, and the mercury precipitated as sulphide. The mercury sulphide is collected and weighed, and the filtrate, containing reduced chlorate, is oxidised with nitric acid, and the chloride estimated volumetrically.

W. P. S.

**Preparation of Inorganic Stannichlorides.** J. G. F. Druce (*Chem. News*, 1918, **117**, 193—196).—A number of stanno- and stanni-chlorides of uni- and bi-valent metals have been prepared. The stannochlorides were obtained by crystallisation of acid solutions containing stannous chloride and the chloride of the second metal. To obtain the stannichlorides, these solutions were first subjected to the action of chlorine. The recorded analyses of the products, in which the water of crystallisation was obtained by difference, show that magnesium and zinc yield anhydrous stannochlorides, whilst those formed by potassium and ammonium contain two molecules of water of crystallisation. The data for the stannichlorides correspond with the following formulæ: $Li_2SnCl_6,8H_2O$; $Na_2SnCl_6,6H_2O$; $K_2SnCl_6$; $Rb_2SnCl_6$; $(NH_4)_2SnCl_6$; $CaSnCl_6$; $SrSnCl_6,4H_2O$; $MgSnCl_6,6H_2O$; $ZnSnCl_6,6H_2O$; $CdSnCl_6$; $CoSnCl_6,6H_2O$; $NiSnCl_6,6H_2O$.

The anhydrous potassium, rubidium, and ammonium stannichlorides are quite stable in the air and do not deliquesce. The alkaline earth stannochlorides are entirely deliquescent, and on this account it was found impossible to obtain a pure specimen of the barium salt.

H. M. D.

**Normal Zirconyl Nitrate.** Ed. Chauvenet and (Mlle.) L. Nicolle (*Compt. rend.*, 1918, **166**, 781—783).—The authors were unable to confirm the existence of a normal zirconium nitrate, $Zr(NO_3)_4,5H_2O$, commonly described in text-books. By evaporating a solution of zirconium hydroxide in nitric acid, even in an atmosphere saturated with nitric acid fumes, they always obtained a zirconyl nitrate, $ZrO(NO_3)_2,2H_2O$, or at temperatures below 10° the *hydrate*, $ZrO(NO_3)_2,3{\cdot}5H_2O$. Attempts to prepare the anhydrous nitrate were not successful, the dehydration being always accompanied by loss of nitric acid.

W. G.

**Basic Zirconyl Nitrates.** Ed. Chauvenet and (Mlle.) L. Nicolle (*Compt. rend.*, 1918, **166**, 821—824).—Zirconyl nitrate, $ZrO(NO_3)_2,2H_2O$ (compare preceding abstract), when dissolved in water, slowly undergoes hydrolysis, and there is slow formation of a precipitate having the composition $ZrO(NO_3)_2,ZrO_2,nH_2O$. A study of the neutralisation by $N/100$-sodium hydroxide of the nitric acid formed during the hydrolysis showed that there are two reactions, namely,

$$2ZrO(NO_3)_2 + 2NaOH = 2NaNO_3 + ZrO(NO_3)_2,ZrO_2 + H_2O$$

and $ZrO(NO_3)_2 + 2NaOH = 2NaNO_3 + ZrO_2 + H_2O$.

When the normal zirconyl nitrate is heated at 120° in the presence of nitric acid vapour, it undergoes dehydration, and at the same time loss of nitric acid, giving a *basic nitrate*, $3ZrO(NO_3)_2,ZrO_2,7H_2O$. If the dehydration takes place in air, there are formed the following basic nitrates: at 110°, $2ZrO(NO_3)_2,ZrO_2,7H_2O$; at 150°, $ZrO(NO_3)_2,2ZrO_2,4H_2O$; at 215°, $ZrO(NO_3)_2,7ZrO_2,5H_2O$; and at 250°, $ZrO(NO_3)_2,10ZrO_2,4H_2O$, and above this temperature zirconium oxide is formed. W. G.

**The Resistance Limits of Mixed Crystals of Vanadium and Silicon with Iron.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 161—179; from *Chem. Zentr.*, 1918, i, 510).—The "resistance limit" is the term given to the composition of mixed crystals at which a sudden alteration occurs in the susceptibility to chemical agents. Whereas it is possible to observe in a direct manner the alterations in the surface of polished pieces of alloys consisting of copper–gold or silver–gold mixed crystals, this cannot be done in the present case, and it is necessary to observe, instead, the effect of various reagents on the metal. After ordinary, slow cooling, mixed crystals of iron and vanadium containing up to 0·43% molecule of the latter are ferromagnetic, whilst mixed crystals richer in vanadium are inactive. Examination was made of the behaviour of the mixed crystals towards solutions of various salts and acids, the resistance limit being found at 0·50 ± 0·05 mol. vanadium.

The iron–silicon mixed crystals gave rather irregular results; solutions of metallic nitrates cause the iron in the mixed crystals to become passive; the action of acids is also somewhat abnormal; copper sulphate, mercuric chloride, gold chloride, and several other salts, together with iodine, indicate a resistance limit at 0·25 mol. silicon, which appears to confirm the existence of the compound FeSi. D. F. T.

## Mineralogical Chemistry.

**The Old and the New Mineralogy.** Sir HENRY ALEXANDER MIERS (T., 1918, **113**, 363—386).—A lecture delivered before the Chemical Society on April 18th, 1918. H. M. D.

**Chemical Composition of Melanophlogites.** E. MANZELLA (*Ann. Chim. Applicata*, 1918, **9**, 91—101. Compare Lasaulx, this Journal, 1876, ii, 54; Bertrand, A., 1881, 1000).—Melanophlogite, a mineral discovered by Lasaulx in association with certain specimens of sulphur, is characterised by its behaviour on heating, changing successively in colour to greyish-yellow, greyish-blue, and deep bluish-black. Purified specimens of various origin recently examined had the following composition: hydrogen, 1·47 to 1·56; carbon, 3·32 to 3·91; silica, 88·76 to 89·12 sulphuric anhydride, 0·63 to 2·49; iron and loss, 0·27 to 0·60; and substances undetermined, 2·67 to 4·94%. A decrease in the proportion of sulphuric anhydride was accompanied by a reduction in the degree of blackening on heating, but other experiments showed that the alteration in colour must be attributed solely to carbonisation of the organic constituents in the mineral. C. A. M.

## Analytical Chemistry.

**Acidimetry of Coloured Solutions. An Application of the Pocket Spectroscope.** ALFRED TINGLE (*J. Soc. Chem. Ind.*, 1918, **37**, 117; *J. Amer. Chem. Soc.*, 1918, **40**, 873—879).—A method is described whereby highly coloured acid solutions may be accurately titrated. The process depends on the fact that the absorption spectra of indicators are different in acid and in alkaline solutions. To make a determination, two similar vessels are taken, one of which contains the solution to be titrated and the other an equal volume of distilled water. To the latter, one drop of standard alkali is added, and then the indicator is slowly added from a burette until the characteristic absorption band shows a sufficiently sharp edge. The position of this edge is noted. Then the same volume of indicator is added to the solution to be estimated, and alkali added from a burette until the characteristic band is observed in the same position. This gives the end-point of the titration. The change does not involve the appearance of a new absorption band, but rather the shifting of a band already present. The method was tested on solutions of sulphuric acid of known concentration, which were coloured by the addition of neutral tea extract or liquorice. The results are quite as accurate as those obtained for colourless solutions by the ordinary method. The amount of indicator used is rather larger than that generally employed; the exact amount necessary must be found experimentally. In the present experiments, 1 c.c. of methyl-orange and 2·5 c.c. of cochineal extract were used. J. F. S.

**Mercuric Oxide as a Standard for Volumetric Analysis.** L. ROSENTHALER (*Zeitsch. anal. Chem.*, 1918, **57**, 98).—Incze has recommended the use of yellow mercuric oxide as a standard in volumetric analysis (A., 1917, ii, 327), but the author points out that he and Abelmann had previously used mercuric oxide for the purpose (A., 1913, ii, 786). W. P. S.

**Detection of Anions.** FRITZ FEIGL (*Zeitsch. anal. Chem.*, 1918, **57**, 135—138).—The substance is boiled with concentrated sodium carbonate solution or fused with a mixture of sodium and potassium carbonates; after filtration, the solution is nearly neutralised with nitric acid and warmed with the addition of an excess of solid zinc nitrate. The mixture is filtered; the precipitate contains zinc sulphide, sulphite, phosphate, borate, fluoride, ferrocyanide, ferricyanide, and cyanide, and also molybdate, vanadate, and tungstate, whilst the filtrate contains zinc thiocyanate, chloride, bromide, iodide, sulphate, thiosulphate, and sulphite. These substances are then identified by drop reactions without further separation. [See also *J. Soc. Chem. Ind.*, July.] W. P. S.

**Estimation of Chlorine in Organic Substances (Gastric Juice, Blood, Milk, etc.).** SIROT and JORET (*Ann. Chim. anal.*, 1918, **23**, 109—113).—The total chlorine in gastric juice is estimated by Volhard's method after the sample has been treated with Esbach's reagent (10 grams of picric acid and 25 grams of acetic acid per litre of water) and filtered. Chlorine in organic and inorganic combination is estimated in the same way after the sample has been evaporated to expel free hydrochloric acid, whilst chlorine in inorganic combination is obtained by titrating the residue left after evaporation and incineration. In the case of blood, sodium metaphosphate is recommended as a clarifier; 20 c.c. of the blood are mixed with 75 c.c. of water, 10 drops of nitric acid, 20 c.c. of 5% sodium metaphosphate solution, and 1·5 c.c. of acetic acid. The mixture is then diluted to 200 c.c., filtered, and the chlorine titrated in the filtrate. The acetic acid–picric acid solution may be used for precipitating the casein, etc., in milk previous to the estimation of the chlorine present. W. P. S.

**Gravimetric Analysis. V. [Chlorides, Bromides, and Iodides.]** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 101—103).—Chlorides, bromides, and iodides are precipitated by a small excess of *N*-silver nitrate in 100 c.c. of the cold solution to which has been added 5 c.c. of *N*-nitric acid, or, in presence of ferric salts, 10—20 c.c. In the case of chlorides and bromides, the mixture is left for one hour and then boiled; in the case of iodides, the silver is added first, the nitric acid after half an hour, and the mixture is boiled after another half-hour. Twenty-four hours later, the precipitate is collected on a plug of cotton wool in a Kelch funnel and dried at 132°. It is washed with 50 c.c. of water acidified with nitric acid, and later with 50 c.c. acidified with acetic acid. Correction values amounting to a few tenths of a mg., according to the weight of the precipitate, are used to improve the accuracy of the results. Iodides may also be precipitated in the presence of hydrochloric acid as palladium iodide. 0·5 Gram of palladium is dissolved in nitric acid and the solution evaporated to dryness several times with hydrochloric acid; the residue is taken up with 10 c.c. of 10% hydrochloric acid, 1 c.c. of alcohol is added to remove any free chlorine, and the solution made up to 100 c.c. In absence of chlorides, the palladium iodide remains in colloidal solution; when precipitated cold, it is flocculent, and becomes granular on heating. With a preponderating quantity of iodide, the neutral solution is diluted so that 100 c.c. will give about 0·1 gram of precipitate; 1·0 gram of sodium chloride is added, and 10 c.c. of palladium chloride solution, with agitation. The liquid is heated until the precipitate becomes granular, and the latter is collected on the cotton filter after twenty-four hours, washed with 100 c.c. of cold water, and dried at 132°. With small quantities of iodide, 100 c.c. of the liquid are acidified with hydrochloric acid and precipitated with 1 c.c. of the palladium solution in the cold. The precipitate is allowed to remain for twenty-four or forty-eight hours, according to its quantity, and is collected in the flocculent condition. The palladium iodide is somewhat soluble in presence of alkali bromides; in presence of large quantities of chlorides, a small correction is applied. J. F. B.

**Titration Method for Chlorine, Bromine, Cyanogen, and Mercury.** Emil Votoček (*Chem. Zeit.*, 1918, **42**, 257—260).—Chlorides may be titrated with standardised mercuric nitrate solution in the presence of a small quantity of nitric acid; 0·06 gram of crystallised sodium nitroprusside is used as the indicator, and the volume of the solution should be about 250 c.c. Sulphates, phosphates, and chlorates do not interfere, but sulphites and nitrites must not be present. The method is trustworthy and more accurate than Volhard's method. [See further, *J. Soc. Chem. Ind.*, July.] W. P. S.

**The Estimation and Distribution of Bromine in the Organs and in the Blood after Dosing with Sodium Bromide.** W. Autenrieth (*Münch. med. Woch.*, 1918, **65**, 33—35; from *Chem. Zentr.*, 1918, i, 472—473).—Bromine in bromides of the alkali metals can be estimated colorimetrically by treating the acidified aqueous solution with potassium hydrogen sulphate and potassium permanganate, the liberated bromine being extracted with chloroform and the extract compared with a standard bromine solution, using the Autenrieth-Königsberger colorimeter. The method is not affected by the presence of chlorine and is especially suitable for small quantities. Organs such as liver, kidneys, brain, etc., are heated in a nickel crucible with pure sodium hydroxide and a little potassium nitrate, and the acidified solution treated in the manner described. Sodium bromide is retained tenaciously by the human organism, and only very slowly eliminated by the kidneys, its retention being favoured by a diet poor in chlorine. The brain shows no specific attraction for bromine. D. F. T.

**Gravimetric and Volumetric Estimation of Fluorine Precipitated as Thorium Fluoride.** F. A. Gooch and Matsusuke Kobayashi (*Amer. J. Sci.*, 1918, [iv], **45**, 370—376).—Investigation of the method described by Pisani (A., 1916, ii, 393) showed that the acidity of the solution and the excess of precipitant are important factors in the estimation of fluorine as thorium fluoride. The acidity of the solution (as free acetic acid) should be from *N*/50 to *N*/5, and the quantity of thorium added should not exceed by more than 50% the amount required for the precipitation. The thorium fluoride may be collected and ignited to oxide, the latter being taken as a measure of the thorium fluoride, $ThF_4,4H_2O$, or the excess of thorium, after filtration, may be precipitated as oxalate and this titrated with permanganate solution (compare this vol., ii, 177). [See, further, *J. Soc. Chem. Ind.*, 391A.] W. P. S.

**Time as a Factor in Gravimetric Analysis. I. Precipitation of Sulphuric Acid.** Z. Karaoglanow (*Zeitsch. anal. Chem.*, 1918, **57**, 77—98).—In the precipitation of sulphuric acid as barium sulphate, the rate at which the barium chloride solution is added has a considerable influence; the most trustworthy results are obtained when the addition is extended over a period of not less than 1·5 minutes. The concentration of the solutions, stirring, concentration of hydrochloric acid, etc., also have an influence, but temperature has little effect. The presence of potassium chloride decreases the amount of barium sulphate found, and to some extent counterbalances the effect of rapid precipitation, but this compensation depends on definite conditions of experiment. W. P. S.

**The Estimation of Sulphates in Urine.** A. L. Flohr (*Arch. Néerland. physiol.*, 1918, **2**, 346—351).—The benzidine method of Rosenheim and Drummond for estimating inorganic and ethereal sulphates gives satisfactory results. If the liquid becomes coloured after hydrolysis of the ethereal sulphates by hydrochloric acid, and the colour interferes with the titration, it can be removed sufficiently by treating the liquid with animal charcoal. S. B. S.

**Estimation of Non-protein Nitrogen in Blood.** Isidor Greenwald (*J. Biol. Chem.*, 1918, **34**, 97—101).—A full account of work previously published (A., 1917, ii, 523). H. W. B.

**New Method for the Direct Nesslerisation of Ammonia in Urine.** James B. Sumner (*J. Biol. Chem.*, 1918, **34**, 37—41).—In the Folin and Denis direct Nesslerisation method (A., 1916, ii, 574), the Merck's blood charcoal may be replaced by copper sulphate. The urine is treated with a practically saturated solution of copper sulphate (298 grams of the crystallised salt per litre). Copper hydroxide is then precipitated by adding a 2·03*N*-sodium hydroxide solution until the neutral point is almost reached, when about 90% of the creatinine is also precipitated. The small amount of creatinine remaining in solution is not sufficient to interfere with the subsequent Nesslerisation.

For rough comparative tests, standard colours similar to those obtained by Nesslerisation are prepared by dilution of a solution containing 6% of crystallised ferric chloride and 2·5% of crystallised cobalt nitrate. H. W. B.

**Apparatus for the Estimation of Nitric Acid by the Schulze-Tiemann Method.** KARL LEUCHS (*Chem. Zeit.*, 1918, **42**, 235).—The decomposition flask is closed with a glass stopper provided with a tapped funnel and a delivery tube, and the stopper is surrounded by a water-seal. The delivery tube, which is bent downwards and under the lower end of the gas-collecting burette, is provided with a glass non-return valve. The whole apparatus is constructed of glass. W. P. S.

**Gasometric Estimation of Nitrates.** C. A. HILL (*Analyst*, 1918, **43**, 215—216).—When an external reaction bottle is used in the estimation of nitrates by shaking the latter with sulphuric acid and mercury, it is necessary to fill the bottle previously with a gas inert towards nitric oxide. Carbon monoxide may be used for this purpose, and is prepared by heating a mixture of sodium formate and concentrated sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, July.] W. P. S.

**New Volumetric Method for the Estimation of Phosphates in Urines.** ARGEO ANGIOLANI (*Giorn. Farm. Chim.*, 1917, **66**, 251—252; from *Chem. Zentr.*, 1918, i, 571).—Twenty-five c.c. of the urine are treated with 1 c.c. of 20% hydrochloric acid, 1 gram of ammonium chloride, and 10 c.c. of a citric acid–magnesium solution (a solution of 35 grams of magnesium oxide in 260 grams of citric acid, the total bulk being 500 c.c., which is then treated with 400 c.c. of 10% ammonia solution and kept for two hours). The precipitate is collected, washed with very dilute ammonia solution, dried at 30—40°, and then dissolved in 50 c.c. of $N/10$-sulphuric acid, of which the excess is then titrated with $N/10$-sodium hydroxide solution, using methyl-orange as indicator. One c.c. of $N/10$-acid is equivalent to 3·55 mg. $P_2O_5$. D. F. T.

**Marsh's Apparatus.** W. KIRKBY (*Pharm. J.*, 1918, **100**, 286).—A tube loosely packed with cotton wool is interposed between the generating flask and the hydrogen jet with the object of preventing any risk of explosion. C. A. M.

**Simple Process for the Estimation of Small Quantities of Arsenic in Corpses.** H. FÜHNER (*Ber. Deut. Pharm. Ges.*, 1918, **28**, 221—229).—The process consists in the destruction of the animal matter by permanganate and sulphuric acid, the distillation of the solution with sodium chloride, and the estimation of the arsenic in the distillate by the Gutzeit method, using mercuric bromide paper. [See *J. Soc. Chem. Ind.*, July.] J. H. J.

**Estimation of Carbon Dioxide in Carbonates by Dittrich's Method.** BÉLA VON HORVATH (*Chem. Zeit.*, 1918, **42**, 121).—Carbon dioxide may be estimated in sodium carbonate or barium carbonate by heating the same at dull redness with borax which has been heated previously at 1000°; the carbonate is decomposed readily, and the loss in weight gives the amount of carbon dioxide present. [See, further, *J. Soc. Chem. Ind.*, 369A.]

W. P. S.

**Filtration of Silica.** P. NICOLARDOT and J. KOENIG (*Ann. Chim. anal.*, 1918, **23**, 104—109).—The fact that a minute quantity of silica passes into the filtrate when hydrated silica is evaporated to dryness and then collected on a filter does not appear to be due to solubility of the silica; the effect of successive evaporations and heating at 110° is to agglomerate the silica so that the whole of it is retained by a good filter. It is recommended that the silica be twice evaporated with hydrochloric acid and heated at 110°, but without intervening filtration, before it is collected; the filtrate may be passed once more through the filter. [See, further, *J. Soc. Chem. Ind.*, July.]

W. P. S.

**Estimation of Strontium.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 80 and 83—84).—*As Sulphate.*—One hundred c.c. of a neutral solution containing 0·5 gram of strontium salt are acidified with 1 c.c. of acetic acid, heated to the boiling point, and 10 c.c. of a 10% solution of sodium sulphate are added. Heating is continued until the precipitate is powdery, when it is left overnight. It is transferred to a Gooch crucible, washed with 50 c.c. of saturated strontium sulphate solution, and weighed after drying at 132°. If the filtrate is required further, alcohol is used as the washing agent. The presence of other salts, especially magnesium chloride and hydrochloric and nitric acids, leads to low results.

*As Carbonate.*—1·0 Gram of potassium nitrate and 10 c.c. of 10% sodium carbonate solution are added to a boiling solution of not more than 0·5 gram of strontium salt in 100 c.c. of solution. Next day the precipitate is washed with 50 c.c. of saturated strontium carbonate solution and weighed as $SrCO_3$ after drying at 132°. Owing to incomplete loss of carbon dioxide on ignition, the precipitate cannot be weighed as oxide.

*As Oxalate.*—The precipitation is made with 10% solution of potassium oxalate, and resembles that of the sulphate. After remaining overnight, the precipitate is washed with saturated strontium oxalate solution. It is dried at 100° for two hours and weighed as $SrC_2O_4,H_2O$, or at 132° for six hours and weighed as $SrC_2O_4$. Other salts, especially magnesium chloride, interfere. This is the most convenient and exact method of estimating strontium.

H. J. H.

**Time as a Factor in Gravimetric Analysis. Precipitation of Barium Chloride with Sulphuric Acid.** Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1918, **57**, 113—121).—In the gravimetric estimation of barium as barium sulphate, sulphuric acid should be used for the precipitation; alkali sulphates must not be used. The acid should be added rapidly; if it is added slowly, the results obtained are too low. [See, further, *J. Soc. Chem. Ind.*, 352A.] W. P. S.

**Volumetric Estimation of Lead by means of Ammonium Molybdate.** LINDT (*Zeitsch. anal. Chem.*, 1918, **57**, 71—76).—In this process, it is essential that an excess of ammonium acetate should be avoided in dissolving the lead sulphate; the results obtained are too high in the presence of such excess, but are trustworthy when the lead sulphate is dissolved in the minimum requisite quantity of the acetate solution. [See, further, *J. Soc. Chem. Ind.*, 352A.] W. P. S.

**Estimation of Copper as Copper Oxide after previous Precipitation as Thiocyanate.** G. FENNER and J. FORSCHMANN (*Chem. Zeit.*, 1918, **42**, 205—206).—The inconvenient drying of the cuprous thiocyanate precipitate to constant weight is unnecessary, and may be avoided by conversion of the precipitate into cupric oxide by roasting in a muffle at a temperature near 800°. [See also *J. Soc. Chem. Ind.*, 391A.] D. F. T.

**Analysis of White Metal.** F. KUREK and A. FLATH (*Chem. Zeit.*, 1918, **42**, 133—134).—Tin is estimated by dissolving the alloy in hydrochloric acid with the addition of ferric chloride, reducing the tin with metallic iron, separating the precipitated antimony and copper, and titrating the filtrate with ferric chloride solution. The antimony and copper are then dissolved in hydrochloric acid to which potassium chlorate is added, excess of free chlorine is expelled by boiling the solution, the two metals are separated as their sulphides, the antimony sulphide is dissolved in sodium sulphide solution, again precipitated in the presence of an excess of oxalic acid, dissolved in hydrochloric acid, the solution boiled until the antimony is reduced, and then titrated with potassium bromate solution. Suitable methods are also described for the estimation of lead, copper, iron, aluminium, nickel, and zinc in the alloy. [See, further, *J. Soc. Chem. Ind.*, 877A.) W. P. S.

**Use of Metallic Silver as a Reducing Agent in the Volumetric Estimation of Iron.** GRAHAM EDGAR and A. R. KEMP (*J. Amer. Chem. Soc.*, 1918, **40**, 777—784).—The reaction between metallic silver and solutions of ferric sulphate in the presence of sulphuric acid and a soluble thiocyanate has been examined. The results obtained show that silver may be employed to effect the complete reduction of the ferric salt provided the dissolved silver is precipitated by thiocyanate. The resulting ferrous solution is filtered, treated with an excess of silver nitrate, and titrated with potassium permanganate. An alternative method consists in titrating the excess of silver nitrate with standard thiocyanate.

The thiocyanate serves to show when the reduction is complete, and further advantages of the method are that silver is usually quite free from iron, that it does not reduce titanium at all, and that it reduces vanadium quantitatively to the quadrivalent condition. [Compare *J. Soc. Chem. Ind.*, 391A.] H. M. D.

**Estimation of Iron in Lactic Acid.** A. HARVEY (*J. Soc. Leather Trades' Chem.*, 1918, **2**, 37—38).—Iron in lactic acid can be estimated very exactly by a colorimetric method in which the colour developed with potassium ferrocyanide is matched against the colour produced by standard iron solution. Potassium thiocyanate is useless. F. C. T.

**Quantitative Separation of Iron from the Cerite Metals in the presence of Calcium.** A. WÖBER (*Zeitsch. landw. Versuchsw. Oesterr.*, 1917, **20**, 500—501; from *Chem. Zentr.*, 1918, i, 476).—A weighed sample is dissolved by prolonged treatment with 2% hydrochloric acid, and to an aliquot portion of the solution there is added tartaric acid in the proportion of approximately four grams to one of the substance. On saturating the solution with hydrogen sulphide and adding aqueous ammonia until a pure black precipitate of iron sulphide is obtained, the transiently precipitated hydroxides of the cerite metals are redissolved. The iron sulphide is treated in the usual manner, whilst the estimation of the cerite metals is effected by the method of Hauser and Wirth (A., 1908, ii, 778). D. F. T.

**Estimation of Nickel with α-Benzildioxime.** R. STREBINGER (*Chem. Zeit.*, 1918, **42**, 242—243).—The author agrees with Grossmann and Mannheim (A., 1917, ii, 391) that Atack's method of estimating nickel by precipitation with α-benzildioxime is trustworthy for small quantities of the metal. When, however, the quantity of nickel exceeds 0·025 gram, the precipitate contains a certain amount of occluded α-benzildioxime, and the results obtained are too high. In such cases, the precipitate should be ignited and the resulting nickel oxide weighed. W. P. S.

**Estimation of Chromium in Chromium Salts, Chrome Liquors, Leather Ashes, and Chromium Residues.** KARL SCHORLEMMER (*Collegium*, 1917, 345 and 371; from *Chem. Zentr.*, 1918, i, 377—378).—The solution of the chromium salt is treated cautiously with approximately *N*-sodium hydroxide until the precipitate has redissolved. Aqueous hydrogen peroxide of approximately 3% concentration is then added, and the solution is boiled until no more oxygen is liberated. The resulting solution is acidified with sulphuric acid, and the amount of chromate estimated by one of the usual volumetric methods. Leather ash or dry chromium residues should be mixed with anhydrous sodium carbonate and magnesium oxide and roasted until yellow, the aqueous extract then being titrated after acidification. For the oxidation of solutions of very impure chromium salts, it is better to use alkaline potassium permanganate solution. The presence of iron in the ash of chrome leather may interfere with the chromium estimation. D. F. T.

**Estimation of Molybdenum.** O. BINDER (*Chem. Zeit.*, 1918, **42**, 255).—When molybdenum is precipitated as sulphide and the latter then ignited to oxide, the oxidation is not complete unless the substance, after preliminary ignition, is treated with nitric acid, evaporated, dissolved in ammonia, reprecipitated with nitric acid, evaporated, and ignited. A correction must be made for any traces of matter which remain insoluble when the ignited oxide is dissolved in ammonia. [See, further, *J. Soc. Chem. Ind.*, July.] W. P. S.

**The Estimation of Molybdenum as Lead Molybdate.** ROBERT STREBINGER (*Oesterr. Chem. Zeit.*, 1917, [ii], **20**, 226—228; from *Chem. Zentr.*, 1918, i, 378).—For the estimation of molybdenum in ferro-molybdenum, 0·5—1 gram is fused with 10 grams of sodium peroxide in an iron crucible. The product is extracted with 500 c.c. of water, and 100 c.c. are taken for the test; after the removal of any iron by the addition of nitric acid and then ammonia solution, the solution is neutralised with acetic acid, boiled, and treated successively with solutions of lead acetate (2—5 grams) with acetic acid (2 c.c.) in 30 c.c. of water, and ammonium acetate (10 grams) in 50 c.c. of water. After boiling for a short time, the precipitate is allowed to settle for six hours. The precipitate is removed by filtration, washed with dilute ammonium acetate solution, dissolved in diluted nitric acid, and reprecipitated by the addition of a solution of ammonium acetate (10 grams) in 50 c.c. of very dilute acetic acid. After twelve hours, the lead molybdate is again separated, washed, dried, and ignited at a moderate temperature before final weighing as $PbMoO_4$. D. F. T.

**A Colour Reaction of Thorium and Zirconium with Pyrogallolaldehyde.** H. KASERER (*Chem. Zeit.*, 1918, **42**, 170).—On the addition of an aqueous solution of pyrogallolaldehyde to one of a thorium compound, a yellow colour is formed, and, after a time, a dirty yellow precipitate is produced, which when filtered off leaves a colourless filtrate. Zirconium compounds, after boiling or after the addition of hydrogen peroxide, give a similar colour and precipitate with cerium compounds; the yellow colour remains after boiling. In the presence of nitric, sulphuric, or hydrochloric acid, a colourless solution and no precipitate are produced. A solution containing only 0·1 mg. of thorium nitrate per 100 c.c. shows the colour clearly. Pyrogallol, pyrogallolcarboxylic acid, and protocatechualdehyde do not give this reaction.

The pyrogallolaldehyde is prepared by dissolving 38 grams of pyrogallol and 36·3 grams of formanilide in absolute ether, condensing this with 15·2 grams of phosphoryl chloride, and filtering after twelve hours. The residue is dissolved in alcohol and precipitated by sodium chloride. The crystals are treated with warm sodium hydroxide, a current of hydrogen is passed through the solution, after which it is acidified and the aldehyde extracted with ether and purified by conversion into the bisulphite compound.

A. B. S.

**Graphic Methods of Analysis.** HANS GRADENWITZ (*Chem. Zeit.*, 1918, **42**, 221).—The composition of such mixtures as formaldehyde, methyl alcohol, and water, and ethyl acetate, alcohol, and water, may be found from the graphs given, the data to be determined being, in the first case, the specific gravity and the formaldehyde content, and in the second, the specific gravity and the ethyl acetate content. [See, further, *J. Soc. Chem. Ind.*, 392A.]

W. P. S.

**Method for Detecting Small Quantities of Chloretone (Trichloro-*tert.*-butyl Alcohol) in Aqueous Solutions.** T. B. ALDRICH (*J. Biol. Chem.*, 1918, **34**, 263—267).—The solution containing the chloretone is subjected to steam distillation. If a large amount of chloretone is present, it crystallises in the cooler part of the condenser in needles. When only small amounts of chloretone are present, crystallisation may not occur, but if the distillate is placed in a small flask fitted with a reflux condenser and boiled for half an hour, needle crystals are then obtained in the condenser when the amount of chloretone exceeds 0·25 mg. If protein is present, it should be digested with pepsin and hydrochloric acid before the steam distillation is carried out. The presence of other organic solvents prevents the crystallisation, and thus interferes with the recognition of chloretone by this method.

H. W. B.

**Estimation of Cholesterol in Blood.** L. KAST, V. C. MYERS, and EMMA L. WARDELL (*Proc. Soc. Exp. Biol. Med.*, 1917, **15**, 1—2; from *Physiol. Abstr.*, 1918, **3**, 31).—One c.c. of blood is extracted with chloroform, and in the extract the cholesterol is estimated colorimetrically by the Liebermann-Burchard reaction (compare *Physiol. Abstr.*, 1917, **2**, 675). The values obtained are lower than those of Bloor, but are believed to be more accurate.

W. G.

**Cammidge's Method for the Estimation of [Reducing] Sugar in Urine.** R. W. GARROW (*Pharm. J.*, 1918, **100**, 148—149).—In estimating sugar by this method (A., 1917, ii, 276), it is noticed in titrating back the excess of iodine with thiosulphate that up to the point where the blue starch iodide is discharged the solution is transparent, but immediately after the first end-point is reached a slight opalescence begins to appear, increasing to a white precipitate of cuprous iodide, and the blue colour returns. The first discharge of the blue colour should be taken as the end-point, and the titration should be done as rapidly as possible. [See, further, *J. Soc. Chem. Ind.*, 276A.]

J. F. B.

**Polarimetric Estimation of Dextrose in Urine.** G. Frerichs and E. Mannheim (*Apoth. Zeit.*, **33**, 34; from *Chem. Zentr.*, 1918, i, 380. Compare A., 1917, ii, 393).—A 100 c.c. flask containing 5 c.c. of lead acetate solution is filled to the mark with the urine and shaken well; the liquid is then filtered and examined in the polarimeter in a 2-dcm. tube, the rotation giving the content of anhydrous dextrose in grams per 100 c.c. of urine. The lead acetate solution should contain 10 grams of the salt and 5 grams of 30% acetic acid in 20 grams of water. If the lead acetate treatment fails to decolorise the urine sufficiently, the latter may be decolorised with charcoal, either at the same time as the lead acetate treatment or subsequently. As the charcoal absorbs a certain proportion of the dextrose, a correction becomes necessary, for which empirical values are given. D. F. T.

**Colorimetric Estimation of Dextrose in Urine.** V. I. Isaacson (*J. Lab. and Clin. Med., St. Louis*, 1918, **3**, 289—294; from *Physiol. Abstr.*, 1918, **3**, 120).—A copper sulphate method, in which the unreduced copper is estimated after adding ammonia in a colorimeter against a standard. S. B. S.

**Estimation of Dextrose in Urine.** C. H. Hugenholtz (*Pharm. Weekblad*, 1918, **55**, 609—614).—A comparison of the iodometric, polarimetric, and fermentation methods of estimating dextrose in urine. The first method is very accurate, the second gives slightly low results, and the values derived from the third method are extremely erratic. A. J. W.

**Estimation of Sugar in Normal Urine.** Stanley R. Benedict and Emil Osterberg (*J. Biol. Chem.*, 1918, **34**, 195—201).—In this method, which permits of the estimation of traces of sugar accurately to within a few thousandths of 1%, the creatinine and polyphenols, and most of the total nitrogen and the glycuronic acid, are first removed from the urine by precipitation with a mercuric nitrate reagent, and the dextrose then estimated colorimetrically after treatment with picric acid. The necessary special reagents are prepared as follows. Mercuric nitrate solution, by adding slowly 220 grams of mercuric oxide to 160 c.c. of concentrated nitric acid until it has dissolved, then boiling, cooling, and adding 60 c.c. of 5% sodium hydroxide solution. It is made up to 1 litre and filtered. Picrate–picric acid solution, by adding 36 grams of picric acid and 400 c.c. of hot water to 500 c.c. of 1% sodium hydroxide solution and shaking until the picric acid has dissolved. It is cooled and made up to 1 litre.

To perform the estimation, 15 or 20 c.c. of the urine are placed in a 500 c.c. beaker, together with an equal volume of the mercuric nitrate solution, and, after mixing, solid sodium hydrogen carbonate is added until frothing ceases and an alkaline reaction to litmus paper is obtained. After filtering, the excess of mercury is removed by adding a pinch of zinc dust and a drop or two of concentrated hydrochloric acid. From 1 to 4 c.c. of the final filtrate (containing about 1 mg. of dextrose) are measured into a large test-tube graduated to indicate 12·5 and 25 c.c. Water is added if required to bring the volume to 4 c.c., and 1 c.c. of 20% sodium carbonate solution is run in, followed by 4 c.c. of the picrate–picric acid solution. The mixture is heated in boiling water for ten minutes, cooled, diluted to the mark, and compared in a colorimeter with a standard solution similarly prepared from 1 mg. of dextrose in 4 c.c. of water or with a permanent standard of picramic acid or potassium dichromate solution. The former is prepared by adding 0·5 c.c. of 20% sodium carbonate solution and 15 c.c. of the picrate–picric acid solution to 105 c.c. of exactly 0·01% picramic acid solution in 0·02% sodium carbonate solution and then diluting to 300 c.c. with water. To prepare the dichromate standard, dissolve 0·536 gram of potassium dichromate in 1 litre of water.

To estimate the fermentable sugar, a second estimation in the urine after fermentation is necessary. About 20 mg. of dextrose and a one-quarter cake of yeast are added to 25 c.c. of the urine. After mixing, it is allowed to remain in an incubator at 35—38° for eighteen to twenty hours. The clear urine is then decanted and the estimation of dextrose carried out as above. The difference between the two estimations gives the fermentable sugar.

H. W. B.

**Modification of the Lewis-Benedict Method for the Estimation of Dextrose in the Blood.** Stanley R. Benedict (*J. Biol. Chem.*, 1918, **34**, 203—207. Compare A., 1915, ii, 111).—The modification consists in adding the solution of picric acid in sodium picrate, employed in the estimation of dextrose in urine (see preceding abstract), instead of picric acid to the laked blood, which renders the subsequent evaporation unnecessary.

H. W. B.

**Sources of Error in the Estimation of Dextrose by the Colorimetric Picrate Method.** T. Addis and A. E. Shevky (*Proc. Soc. Exp. Biol. Med. New York*, 1918, **15**, 79).—The reddish-brown colour produced on heating dextrose, picric acid, and sodium carbonate varies with the temperature, duration of heating, and amount of carbonate present. G. B.

**Inversion and Estimation of Sucrose.** A. R. Rose (*Proc. Soc. Exp. Biol. Med. New York*, 1917, **15**, 16—17).—Heating for ten minutes at 100° with 2 volumes of saturated picric acid inverts the sucrose; then 1 vol. of 20% sodium carbonate is added, and after a further twenty minutes' heating the total dextrose + lævulose is estimated colorimetrically according to Lewis-Benedict. The amount originally present is estimated in a similar tube, in which the sodium carbonate was added before heating. The difference between the two tubes represents invert-sugar (compare preceding abstract). G. B.

**Estimation of Furfuroids (Furfurosans) in the Different Products of Beet Sugar Factories. I.** R. Gillet (*Bull. Assoc. chim. Sucr. Dest.*, 1917, **35**, 53—62).—It is known that other substances besides pentoses and pentosans yield more or less furfuraldehyde under the well-known conditions of distillation with hydrochloric acid. Chalmot has stated that sucrose yields not more than 0·2%, but the author, operating on 5—20 grams of pure sucrose, has obtained from 0·38 to 0·75%. of furfuraldehyde under the Tollens-Councler conditions of working. The method of procedure is described fully, and attention is directed to certain points which are of importance in securing uniform results. To prevent superheating, the distillation flask should not be immersed in the bath below the level of the liquid in the flask. The temperature of the bath should be such as to produce uniform distillation at the rate of 30 c.c. in twelve to fourteen minutes; when operating on 10 grams of sucrose, the author found it necessary to heat the bath to 155—160°, since at lower temperatures distillation was slow and the distillate was often cloudy, owing to the presence of an unknown, yellow substance in suspension. Great importance is attached to strict adherence to the prescribed method of replenishing the acid during distillation, exactly 30 c.c. being added as soon as 30 c.c. has distilled. In spite of attention to these and other details of procedure, it was found impossible to secure absolutely uniform yields of furfuraldehyde from sucrose. J. H. L.

**Colour Reaction for Ground Wood Pulp or the Incrusting Matters of Wood with Phenylhydrazine Hydrochloride.** S. Jentsch (*Zeitsch. angew. Chem.*, 1918, **31**, 72).—An aqueous solution of phenylhydrazine hydrochloride gives an intense orange-yellow coloration with raw wood fibre, which subsequently changes to a characteristic bright green on drying in presence of air; the appearance of the green colour is accelerated by suitable heating. Cotton and other pure cellulose fibres are stained only to a pale yellow, which changes to a characteristic light brown after drying. The above test for lignocellulose is stated to be sharper and more definite than the phloroglucinol–hydrochloric acid test. [See also *J. Soc. Chem. Ind.*, 365A.] J. F. B.

**New Reaction of Formic Acid and Hyposulphites.** E. Comanducci (*Boll. chim. farm.*, 1918, **57**, 101—102).—The presence of formic acid in a liquid may be detected by heating the latter gently with concentrated sodium hydrogen sulphite solution until gas bubbles begin to escape, the liquid being then cooled and fresh, dilute sodium nitroprusside solution poured carefully on to its surface; a green or blue ring is thus formed, hydrogen cyanide being liberated at the same time. The blue precipitate, $Na_4Fe_2(CN)_9$, results from the interaction of the nitroprusside and sodium hyposulphite, the latter being formed by the action of the formic acid on the sodium hydrogen sulphite (compare A., 1904, ii, 845). T. H. P.

**Estimation of Lactic Anhydrides in Lactic Acid.** F. C. Thompson and Kyohei Suzuki (*J. Soc. Leather Trades' Chem.*, 1918, **2**, 115—121).—Lactide reacts completely in the cold with alkali hydroxide in ten minutes if the alkali is in considerable excess. No heating is therefore necessary in the analysis of lactic acid. Furthermore, the proportion of lactide present in lactic acid depends on the dilution and time of keeping, so that analytical results do not indicate the amount of lactide in a dilute solution used in technical practice, for example, in deliming hides. [See, further, *J. Soc. Chem. Ind.*, 343A.], F. C. T.

**An Optical Method for the Estimation of Malic and Tartaric Acids in the same Solutions.** J. J. Willaman (*J. Amer. Chem. Soc.*, 1918, **40**, 693—704).—The method depends on the facts that uranyl acetate enhances the rotation of *l*-malic and *d*-tartaric acids, whilst ammonium heptamolybdate reverses the direction of the rotation in the case of *l*-malic acid, giving strongly positive solutions in each case. A chart is made connecting the rotations of solutions, containing up to 1% of the acids, activated by uranyl acetate on the one hand (the curves slope down from left to right) with those of solutions activated by ammonium heptamolybdate on the other (the curves slope up from left to right). The point of intersection of a given pair of curves will give, therefore, the number of grams of tartaric acid on the abscissæ and the proportion of malic acid on the ordinates.

The details of the method are based on Yoder's work on malic acid (A., 1911, ii, 1141) and further developments by Gore and others in America, which have been embodied in an official process (*J. Assoc. Off. Agric. Chemists*, 1916). An amount of the sample is taken which, judged by titration, will contain at least about 0·1 gram of either acid and not more than 0·6 gram of tartaric acid or 0·8 gram of malic acid. This is neutralised with *N*-ammonia solution, mixed with 2 vols. of 95% alcohol, filtered from pectins, and the filtrate slowly mixed with an excess of a 10% solution of barium chloride in 50% alcohol, and then made up to fourteen times the original volume with 95% alcohol. The precipitate is collected by centrifuging, boiled with water, mixed with 10 c.c. of 20% ammonium sulphate solution, the mixture is concentrated to about 80 c.c., cooled, mixed with 6 c.c. of glacial acetic acid, and diluted to 100 c.c. Two 25 c.c. portions of the clear solution, after centrifuging, are taken, mixed with 10 c.c. of an 8% solution of pure uranyl acetate and 10 c.c. of 10%

ammonium heptamolybdate respectively, left for three hours in the dark, and then polarised at about 20° in a 2-dcm. tube. If the molybdate solution becomes green through reduction, a drop of bromine water may be added. J. C. W.

**Estimation of Fatty Acids in Butter Fat.** E. B. Holland and J. P. Buckley, jun. (*J. Agric. Research*, 1918, **12**, 719—732).—Direct esterification of butter fact (with absolute alcohol containing hydrogen chloride or concentrated sulphuric acid). and subsequent fractional distillation of the resulting esters, affords a trustworthy method for the estimation of certain of the fatty acids. The following quantities of fatty acids were found in butter fat: hexoic acid, 1·36%; octoic acid, 0·975%; decoic acid, 1·831%; lauric acid, 6·895%; myristic acid, 22·618%. Butyric acid (3·153%) and palmitic acid (19·229%) were estimated by difference, stearic acid (11·384%) by crystallisation, and oleic acid (27·374%) from the iodine number of the insoluble fatty acids. [See, further, *J. Soc. Chem. Ind.*, 846A.] W. P. S.

**Test for Acetone in Urine.** M. Wagenaar (*Pharm. Weekblad*, 1918, **55**, 57—60).—The presence of 0·5 mg. of acetone in 10 c.c. of urine can be detected by mixing the sample with a solution of acetic acid, tartaric acid, and sodium nitroprusside, and covering the liquid with a concentrated solution of ammonia. A coloration like that of permanganate solution is developed at the junction of the liquids. A. J. W.

**Detection of Acetone in Urine.** P. Bohrisch (*Pharm. Zeit.*, 1918, **63**, 173—174. Compare this vol., ii, 179).—The author finds that Legal's test is more sensitive than Lange's ring test, and mentions that Arends and Urban had shown in 1911 that it was not necessary for the sodium nitroprusside solution used in the tests to be freshly prepared. W. P. S.

**Detection of Arbutin.** Hans Salomon (*Ber. Deut. pharm. Ges.*, 1918, **28**, 138—139).—The tests commonly applied for arbutin in urine, for example, after the ingestion of bearberry leaf tea, are not specific to this substance. D. F. T.

**Direct Estimation of Urea and Ammonia in Placenta Tissue.** Frederick S. Hammett (*J. Biol. Chem.*, 1918, **33**, 381—385. Compare Sumner, A., 1916, ii, 655).—The methods of estimation recommended by the author are essentially those devised by Sumner (*loc. cit.*), the chief modification being the addition of potassium carbonate in a solid form to liberate the ammonia prior to aeration. H. W. B.

**Estimation of Uric Acid in Urine and Blood.** D. G. Cohen Tervaert (*Arch. Néerland. physiol.*, 1918, **2**, 337—345).—In the case of urine, the uric acid is precipitated by ammonium chloride as ammonium urate under conditions described by the author in detail. The precipitate is washed with ammonium chloride by centrifugalisation, then dissolved in lithium carbonate solution, and the uric acid is estimated colorimetrically by Folin's phosphotungstate reagent in a solution made alkaline by sodium carbonate. In the case of blood, the proteins are separated by coagulation of the solution acidified by acetic acid, the filtrate is concentrated to a small bulk, and the uric acid is precipitated as urate and the amount estimated in a manner similar to that described for the estimation of uric acid in urine. S. B. S.

**Estimation of Uric Acid in the Blood by Titration with Permanganate.** J. Lucien Morris (*Proc. Amer. Soc. Biol. Chem.*, 1917, xxi; *J. Biol. Chem.*, 1918, **33**. Compare A., 1917, ii, 279).—The uric acid from 20 c.c. of blood is isolated as zinc urate. It is then dissolved in hydrochloric acid and disodium hydrogen phosphate added until all the zinc is reprecipitated. A saturated solution of sodium hydrogen carbonate (25 c.c.), 10% potassium iodide (5 c.c.), and 0·5% starch solution (1 c.c.) are added, and 0·002*N*-permanganate run in from a burette until the blue colour of iodide of starch appears. In the slightly alkaline solution, the oxidation of the potassium iodide, and consequent production of the blue iodide of starch, does not occur until all the uric acid has been oxidised. The results are accurate to within 5%. H. W. B.

**Homatropine and the Vitali Test.** H. Droop Richmond (*Analyst*, 1918, **43**, 167—168).—Although the Vitali test serves to distinguish homatropine or its hydrobromide from atropine, hyoscyamine, or hyoscine, it is untrustworthy when applied to homatropine sulphate, since the sulphuric acid in this salt causes the production of a violet coloration. In testing the sulphate, the alkaloid should be isolated and the reaction applied to it instead of to the original salt. W. P. S.

**Microchemical Tests for Choline.** N. Schoorl (*Pharm. Weekblad*, 1918, **55**, 363—369).—A description of the microchemical characteristics of double salts of choline hydrochloride with platinum chloride, gold chloride, mercuric iodide, bismuth iodide, and of the picrate and picrolonate. A. J. W.

**Estimation of Creatinine and of Creatine in the Blood.** Isidor Greenwald and Grace McGuire (*J. Biol. Chem.*, 1918, **34**, 103—118).—The new method consists in removing the blood-proteins by heat coagulation in dilute acetic acid solution, and then shaking with kaolin, which almost completely removes the creatinine, leaving the creatine unaffected. After filtration and concentration, the creatine is hydrolysed by hydrochloric acid and estimated by Folin's colorimetric method. H. W. B.

**Detection and Estimation of Quinine in Blood and Urine.** W. Ramsden and I. J. Lipkin (*Ann. Trop. Med. Parasitol*, 1918, **11**, 443—464).—The thalleioquinine reaction is rendered more delicate

(1:40,000 with certainty) by adding to 10 c.c. of the quinine solution, feebly acidified with hydrochloric acid and shaken in a test-tube, one-tenth saturated bromine water drop by drop until the pale yellow colour is no longer instantly discharged (white background). At intervals of five seconds, lots of about 2 c.c. are poured into test-tubes containing one drop of concentrated ammonia. Finally, all ammonia solutions are mixed, and the green pigment is extracted with chloroform. The Herapath test may, with Christensen's reagent and a polarising microscope, be employed for the recognition of 1/500 mg. of quinine. Mayer's reaction (ordinarily 1:500,000) may be rendered twenty times as delicate by extracting the alkaloid with ether free from all traces of aldehyde or acetone, dissolving in saturated ammonium sulphate solution, and adding 1/100 volume of the reagent. Potassium tri-iodide (limit, 1:1,500,000) is less suitable, on account of the colour; phosphotungstic acid and bismuth potassium iodide are much less delicate.

Blood is boiled with ammonium sulphate, urine is precipitated with lead acetate and ammonium sulphate in the presence of acetic acid; in either case, after addition of ammonia to the filtrate, the quinine is extracted with ether free from ketones, the ether is evaporated, and the residue is dissolved in saturated ammonium sulphate solution (at least 10 c.c. for each mg. of quinine). The turbidity due to Mayer's reagent is compared nephelometrically with that in saturated ammonium sulphate solutions containing known amounts of quinine (gauged test-tubes in box with slit for illumination, dark-room, best dilution of quinine 200—300 c.c. per mg.). Thus 0·02—0·03 mg. of quinine in 5 c.c. of blood may be estimated with an error of less than 5%. Larger quantities of quinine (100 mg.) may be precipitated as periodide, from which the quinine is recovered with sodium hydrogen bisulphite and ether, so that it may be weighed or titrated. Gordin's volumetric method (A., 1900, ii, 114, 777; 1907, ii, 487; 1902, ii, 186) is found to be accurate. G. B.

**Detection of Proteins by Bleaching Powder and Hydrochloric Acid.** ADOLF JOLLES (*Deut. med. Woch.*, **43**, 1620—1621; from *Chem. Zentr.*, 1918, i, 303—304).—The test mentioned in the title is not sufficiently sensitive, and can be replaced by the following "three-tube test." The specific reagent contains 10 grams of mercuric chloride, 20 grams of citric acid, and 20 grams of sodium chloride in 500 c.c. of water. To three tubes are added 5 c.c. of filtered urine, to the first tube 1 c.c. of 30% acetic acid + 5 c.c. of the reagent; to the second, 1 c.c. of acetic acid + water, and to the third, water only. All tubes are made to contain the same volume of liquid. By comparing differences in the turbidities after remaining for ten minutes, it is possible to ascertain whether traces of proteins are present. S. B. S.

# General and Physical Chemistry.

**Optics of Disperse Systems. II.** I. Lifschitz and Jens Brandt (*Kolloid Zeitsch.*, 1918, **22**, 133—143. Compare this vol., ii, 181).—The refractive power of disperse systems has been examined by observations on colloidal solutions of sulphur and on soap solutions.

The results obtained with colloidal solutions of sulphur, fractionated by the method described by Odén, show that the refractive index increases with the concentration of the solution (grams per 100 c.c.) according to a linear equation. The density of the sols also increases with the concentration in an approximately linear manner. The value of $(d_s - d_0)/c$, in which $d_s$ is the density of a sol of concentration $c$ and $d_0$ the density of the solvent, is, however, much greater than for solutions of sulphur in carbon disulphide in which the sulphur is present in the molecular condition. The refractivity, measured by Gladstone and Dale's formula, is much more nearly constant than it is when the formula of Lorenz and Lorentz is employed.

The results obtained in measurements of the refractive index of aqueous solutions of sodium oleate, palmitate and stearate, and of potassium palmitate at 70° show that the refractive index changes with the concentration according to a linear formula. The molecular refractivities of the soaps appear to be independent of the concentration, and consequently of the degree of dispersity and of the extent to which the soaps are hydrolysed and dissociated.

H. M. D.

**Effect of an Electric Field on the Spectrum Lines of Helium.** Toshio Takamine and Usaburo Yoshida (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 325—334).—The mode of resolution of the lines $\lambda$ 5048, $\lambda$ 5016, $\lambda$ 4922, $\lambda$ 4472, $\lambda$ 4438, $\lambda$ 4388, and $\lambda$ 4121 under the influence of electric fields varying in intensity between 3000 and 70,000 volts per cm. is described. With the exception of $\lambda$ 4686, the resolution of all the helium lines examined has been found to be unsymmetrical with respect to the initial line.

H. M. D.

**Effect of an Electric Field on the Spectrum Lines of Hydrogen. II.** Toshio Takamine and Usaburo Yoshida (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 321—323. Compare A., 1917, ii, 402).—The changes produced by the action of a strong electric field have been examined by the investigation of a further series of hydrogen lines. The photographs show that the outer components of the lines belonging to the Balmer series frequently extend into the region of the unaffected secondary lines. The apparent lack of any connexion between the two groups of lines suggests that they are due to different carriers. H. M. D.

**Effect of an Electric Field on the Spectrum Lines of Hydrogen.** SHIGEHARU NITTA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 349—355. Compare preceding abstract).—The Stark effect has been examined with electric fields of considerably greater intensity than those used by previous observers. The $H_\beta$ line yields six components, the separation of which is proportional to the intensity of the field. In addition to the Balmer lines, certain lines belonging to the secondary spectrum were investigated. H. M. D.

**Optical Investigations on the Constitution of the Nitrates.** KONR. SCHAEFER (*Zeitsch. wiss. Photochem.*, 1918, **17**, 193—217. Compare A., 1910, ii, 562; 1917, ii, 61, 186).—The ultra-violet absorption of aqueous solutions of various nitrates has been examined over a considerable range of concentration. The results obtained for glucinum, silver, thallous, copper, mercurous, cerous, bismuth, and thorium nitrate are shown in the form of logarithmic absorption curves. On examining the available data for the nitrates, it would seem that these may be divided into three groups according to their optical behaviour at different concentrations. The nitrates of the alkali and alkaline earth metals satisfy the requirements of Beer's law. This relation is only approximately satisfied by the nitrates of glucinum, magnesium, aluminium, manganese, zinc, cadmium, lead, cobalt, and nickel, which form the second group. The deviations are partly due to hydrolysis and in part to the superposed absorption effect of the metal. To the third group belong the nitrates of metals which show large divergences from Beer's law. The absorption of the nitrates in this group (copper, silver, thallous, mercurous) increases rapidly with increase in the concentration of the solutions. This grouping of the metallic nitrates shows an undoubted connexion between the optical properties and the electro-affinity of the metals. The nitrates of the strongly electropositive metals show the selective absorption which has been attributed to that arrangement of the atoms which is found in the nitrate ion, as distinguished from the non-selective absorption of the grouping which is characteristic of the organic nitrates and of concentrated nitric acid. The absorption exhibited by the nitrates of the weak electropositive metals cannot be satisfactorily explained in terms of these two forms of the nitrate group, and it is suggested that the optical behaviour affords evidence of a third configuration of the atoms in the nitrate group.

The absorption of fused potassium nitrate has also been examined, and the selective absorption which it exhibits resembles closely that found for aqueous solutions of the alkali nitrates. In this respect it differs markedly from the absorption of anhydrous nitric acid, which shows no selective effect, although this is shown by dilute aqueous solutions of the acid. H. M. D.

**Spectral Reaction of Methylfurfuraldehyde and β-Hydroxy-δ-methylfurfuraldehyde.** (KINTARŌ OSHIMA and TETSUTARŌ TADOKORO (*J. Tokyo Chem. Soc.*, 1918, **39**, 23—30. Compare Oshima and Tollens, A., 1901, ii, 484).—A comparison of the absorption spectrum of samples of hydroxymethylfurfuraldehyde (as phloroglucide in hydrochloric acid solution) from various sources shows identity of the substance prepared by Kiermayer's method with that obtained from dextrose, lævulose, or inulin by distillation with hydrochloric acid. With hydroxymethylfurfuraldehyde prepared from galactose and lactose, the absorption band is shifted a little towards the F-line, and even slightly overlaps that line in the case of samples prepared from sucrose. These different absorption spectra can, however, be readily distinguished from that given by methylfurfuraldehyde. S. H.

**The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. The Influence of certain Inorganic Haloids on the Optical Rotatory Powers of α-Hydroxy-acids, α-Amino-acids, and their Derivatives.** GEORGE WILLIAM CLOUGH (T., 1918, **113**, 526—554).—The author has compared the effect of sodium haloid salts on the optical rotatory powers of *l*-lactic, *d*-glyceric, *l*-malic, and *d*-tartaric acids and certain of their esters, and the effect of introducing a given radicle into the molecules of the configuratively similar hydroxy-acids, *l*-lactic, *l*-glyceric, *d*-malic, and *d*-tartaric acids, and from his results assumes that the optical rotatory powers of similarly constituted compounds possessing the same configuration are in general influenced similarly by the same changes in the external conditions and also by the introduction of the same substituent into a given radicle attached to the asymmetric carbon atom. The rotatory powers of the above four acids and of *d*-α-hydroxybutyric, *l*-α-hydroxy*iso*valeric, *d*-α-hydroxy*iso*hexoic, *d*-α-hydroxy-β-phenylpropionic, and *d*-α-hydroxyglutaric acids and their derivatives indicate that all these acids possess the same relative configurations, and they are designed as "*d*"-acids. Of the naturally occurring α-amino-acids, it is similarly assumed that *d*-alanine, *l*-serine, *l*-aspartic acid, *d*-valine, *l*-leucine, *d*-*iso*leucine, *d*-α-aminobutyric acid, *d*-glutamic acid, *l*-phenylalanine, and *l*-tyrosine all possess the same configurations, denoted by the symbol "*l*." The dextrorotatory (*d*-) α-halogen acids which have been isolated are assumed to be configuratively similar compounds and related configuratively to the "*l*"-amino-acids, which it is suggested are enantiomorphously related to the "*d*"-hydroxy-acids. This is supported by a comparison of the rotatory powers of the optically active α-bromoacylamino-acids with those of the α-aminoacylamino-acids. W. G.

**The Radioactivity of the Waters of Neuchâtel and Seeland.** H. PERRET and A. JAQUEROD (*Arch. Sci. phys. nat.*, 1918, [iv], **45**, 277—297, 336—348, 418—437).—The content in radium emanation of the spring waters in a very small region, the Neuchâtel Jura mountains and neighbourhood, has been exhaustively studied. Then a minute parallel study of two regions, each of only a few square kilometres, and, lastly, the prolonged parallel study of two springs in the same district and then in different districts, were carried out. More than a hundred springs were examined. The radioactivity of these springs is feeble and varies between 0 and $3 \cdot 5 \times 10^{-10}$ curie of emanation per litre, the quantity varying in all the springs considerably with the time. No relation was found between radioactivity and the volume of flow of the spring or its temperature, and the few thermal and mineral springs found were not especially radioactive. In passing across the Jura chain from S.E. to N.W., there is a marked increase in the radioactivity of the water. The crystalline rocks beneath come nearer to the surface in travelling in this direction. The two springs examined continuously showed maxima and minima of radioactivity recurring at the same intervals of time. The quantity of radioactive salts in the waters was too small to be detected. F. S.

**Sign of the Zinc Electrode.** WILDER D. BANCROFT (*J. Physical Chem.*, 1918, **22**, 371—379).—A theoretical paper in which the sign given to potential values is discussed. It is pointed out that with electrodes which form cations, the *E.M.F.* is a measure of the difference of the chemical potentials, but has the opposite sign; with electrodes which form anions, the two potentials have the same sign. Since the electrical potential of the copper in a Daniell cell is higher than that of the zinc, and since the zinc electrode is the place of lowest electrical potential, although highest chemical potential, it follows that the minus sign ought to be used when writing the potential difference $Zn|ZnSO_4$. This is in keeping with the practice of physicists and physical chemists.

J. F. S.

**Photochemical Cell, containing Complex Cyanides of Nickel or Platinum.** SATOYASU IIMORI (*J. Tokyo Chem. Soc.*, 1918, **39**, 1—13).—A photochemical cell was constructed with platinum electrodes, which were immersed in a solution of potassium nickel cyanide or potassium platinocyanide, one only of the electrodes being exposed to light. In this cell the electrode exposed to light is positive, but in a photochemical cell containing a solution of potassium ferrocyanide, previously described by the author (*ibid.*, 1917, **38**, 507), it was negative. The current from the present cell decays rapidly when the circuit is closed, notwithstanding the insertion of a considerable resistance, but in the former cell a constant current was obtained during the exposure to light. The cause of the *E.M.F.* of this cell is not yet known with certainty, but it would seem not to be the photoelectrical effect on the electrode, as it is not observed when the complex cyanides are replaced by other salt solutions. S. H.

**Method for Determining the Temperature of Luminous Flames.** Hermann Senftleben and Elisabeth Benedict (*Physikal. Zeitsch.*, 1918, **19**, 180—181).—The temperature of luminous flames is obtained by inserting thin platinum or gold wires into the flame and estimating the temperature of the wires by means of a Holborn-Kurlbaum pyrometer. To compensate for the loss of temperature occasioned by the insertion of the wire, it is raised to the temperature of the flame by the passage of an electric current. When the wire and flame are exactly at the same temperature there is no deposition of carbon, but if the temperature of the wire is lowered slightly there is an immediate deposition of carbon. To correct, if necessary, for the change of temperature brought about by change in the shape of the flame owing to the insertion of the wire, measurements were made with wire of varying diameters (0·2—1·0 mm.), and it was shown that only at greater diameters than these does the temperature depend on the thickness of the wire. The temperature of the middle of a Hefner lamp flame determined by this method is found to be 1690° abs., which is about the mean of the previously recorded values (1680—1711°). J. F. S.

**Improved Form of Thermo-regulator.** John B. Ferguson (*J. Amer. Chem. Soc.*, 1918, **40**, 929—930).—The adjustment of the level of the mercury in the regulator tube is made by means of a plunger, and the mercury makes contact with a fixed platinum wire. H. M. D.

**Thermo-regulator for Apparatus fitted with a Constant Water-level.** Jaroslav Milbauer (*Zeitsch. anal. Chem.*, 1918, **57**, 162—164).—The overflow water from the apparatus is conducted into one limb of a U-tube, the lower part of which is constricted and filled with mercury; the excess of water leaves the upper end of the limb of the U-tube through a side tube, a small by-pass being also fitted at the lower part of the limb. The other limb contains a floating valve, the lower end of which rests on the surface of the mercury. Should the supply of water be interrupted, the limb of the U-tube empties through the by-pass, decreasing the pressure on the mercury, and the valve falls, thus cutting off the supply of gas to the burner under the apparatus.

W. P. S.

**Cineole as a Solvent in Cryoscopy.** Charles E. Fawsitt and Christain H. Fischer (*J. Roy. Soc. New South Wales*, 1918, **51**, 467—472).—Cineole is an oil of the formula $C_{10}H_{18}O$ which occurs largely in oil of eucalyptus. It is extracted by simple freezing. This substance has b. p. 175—176°, m. p. 0·9°, it is very hygroscopic, and the presence of water in the product accounts for the m. p. −1° usually given. Cineole is not generally useful as a cryoscopic solvent, chiefly on account of its hygroscopic properties, but in some cases it is found to be a more suitable solvent than benzene, although somewhat more difficult to work with. It has a cryoscopic constant 6·7 and a latent heat of fusion 22·2 cal. per gram. J. F. S.

**The Saturated Vapour Processes of Penta-atomic Substances.** E. ARIÈS (*Compt. rend.*, 1918, **166**, 935—939).—Taking Young's values for the physical constants of stannic chloride, the author deduces the formula $\Pi = \tau^{20/7}Z/x$, where

$$x = \{1 + (1-\tau)(0{\cdot}84-\tau)/[1{\cdot}8(1-\tau)^2 + 0{\cdot}9]\}\tau^{13/7}$$

for the saturated vapour pressures of penta-atomic substances. The values calculated from this formula for methyl fluoride are in fairly close accord with those observed by Collie, except at a temperature of $-5°$. There is not such close agreement in the case of chloroform with the values as obtained by Regnault unless the critical constants of chloroform are taken as 247° and 45·26 atmos. W. G.

**Rapid Pressure Method for the Determination of Molecular Weights and Hydrogen Equivalents.** W. H. CHAPIN (*J. Physical Chem.*, 1918, **22**, 337—344).—A modification of the vapour density method of determining molecular weights by measuring the pressure set up by a known weight of vapour in a known volume at a measured temperature. The apparatus used consists of a 500 c.c. distilling flask the side tube of which is replaced by a mercury manometer. The manometer tube is 5 mm. diameter and 20 cm. high, and is fitted with a sliding celluloid scale. The top of the flask is fitted with the usual device for dropping in the substance at the right moment. The method is available for all liquids boiling below 90°. The substance is volatilised by steam, and as the whole of the apparatus is not at a uniform temperature, the average temperature must be computed. A method for deducing the average temperature is indicated. The usual precautions are taken in making the pressure measurement. An interesting innovation is introduced in the use of gelatin capsules for weighing the substance under investigation.

The same apparatus can be used for the determination of the equivalents of the metals zinc, aluminium, sodium, calcium, and magnesium. In all cases except sodium, weighed quantities of the metals are dropped into a measured volume of *N*—3*N*-hydrochloric acid contained in the bulb of the apparatus; with sodium, alcohol is used. J. F. S.

**Heat of Formation of the Anhydrous Calcium Borates.** R. GRIVEAU (*Compt. rend.*, 1918, **166**, 993—995).—The pure anhydrous calcium borates were prepared by adding the calculated quantity of calcium carbonate to fused boric anhydride. The heat of solution of each of these borates in *N*/2-hydrochloric acid was then determined, and from these results the heat of formation of each borate was calculated, the results obtained being given by the equation:

$2B_2O_3$ sol. + CaO sol. = $2B_2O_3,CaO$ sol. + 39·8 cal.
$B_2O_3$ sol. + CaO sol. = $B_2O_3,CaO$ sol. + 30·9 cal.
$B_2O_3$ sol. + 2CaO sol. = $B_2O_3,2CaO$ sol. + 48·5 cal.
$B_2O_3$ sol. + 3CaO sol. = $B_2O_3,3CaO$ sol. + 62·2 cal.

The energy of combination of each successive molecule of calcium oxide with two molecules of boric anhydride diminishes from 39·8 cal. to 13·7 cal. W. G.

**Apparatus for Cleansing Pyknometers.** MARCEL DUGARDIN (*Ann. Chim. anal.*, 1918, **23**, 125—126).—A narrow glass tube, connected with a flask and a water-pump, is passed down the neck of the pyknometer so that the contents of the latter may be drawn off; water is then admitted to the pyknometer and drawn off again by means of the narrow tube. W. P. S.

**Adsorption Compounds.** R. HALLER (*Kolloid Zeitsch.*, 1918, **22**, 113—133).—The formation of adsorption compounds by the interaction of dyes with other substances has been examined. Towards chemically indifferent solvents, adsorption compounds behave like mechanical mixtures. Adsorption compounds with a colourless adsorbent when dissolved in a suitable solvent show the same absorption spectrum as the corresponding solution of the dye. The melting points of adsorption compounds containing an adsorbent of low melting point are not very different from the melting point of the adsorbent. The general physical behaviour of the so-called adsorption compounds leads, therefore, to the conclusion that these are to be regarded as mechanical mixtures. [Compare *J. Soc. Chem. Ind.*, 411A.] H. M. D.

**Certain Relations between Crystalline Form, Chemical Constitution, and Optical Properties in Organic Compounds.** EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1918, **8**, 277—285, 319—327).—In the expectation that there should be discoverable some relationship between the optical and the geometrical constants of crystals, an investigation has been made of a number of organic substances typical of the different classes of the tetragonal system. Making use of the Lorentz-Lorenz expression $(n^2-1)/(n^2+2)$, the author calculates refractivity constants $R'_\omega$ and $R_\epsilon$ for the two principal refractive indices $\omega$ and $\epsilon$, and finds that, in a number of cases, the ratio of these constants is almost exactly equal to the reciprocal of the crystallographic axial ratio in the corresponding directions in the crystal structure. Thus in the case of carbamide (tetragonal scalenohedral), $R_\omega/R_\epsilon = 0{\cdot}834$, $a:c = 0{\cdot}833$; in pentaerythritol (ditetragonal pyramidal), $R_3/R_\epsilon = 1{\cdot}07$, $a:c = 1{\cdot}024$; and in mellite, $C_6(CO_2)_6Al_2,18H_2O$ (ditetragonal bipyramidal), $R_\omega/R_\epsilon = 1{\cdot}046$, $a:c = 1{\cdot}055$. A similar relation holds in the double propionates of calcium with strontium and lead, and in isomorphous mixtures of the latter with the corresponding cubic calcium–barium double salt. It is pointed out that the refraction ratios, as well as the crystallographic axial ratios, are connected with the spacing of the planes of atoms in the space-lattices of the substances, and that comparison of the two ratios may be expected to throw light on the type of space-lattice represented in each case. Skeleton space-lattices are suggested for the above-mentioned substances. A number of exceptions to the rule of inverse proportionality occur In some cases the deviation is due to an incorrect choice of axial ratios; in others it may be attributed to the presence of asymmetric carbon atoms or to atomic anisotropism. E. H. R.

**Liquid Crystals of the Hydrates of 10-Bromophenanthrene-3- or -6-Sulphonic Acid.** O. LEHMANN (*Ann. Physik.*, 1918, [iv], **55**, 81—102).—In the solid state, the compound forms thin leaflets belonging apparently to the rhombic system, only slightly soluble in hydrochloric acid, from which it was recrystallised, easily soluble in alcohol, but with decomposition and separation of slender needles. The compound forms two liquid crystalline hydrates with water, the one with little water being slimy or gelatinous, that with more water forming separate liquid crystalline drops. The two forms appear to form mixed crystals to a limited extent. The liquid drops have been examined microscopically in great detail, both with ordinary and polarised light, and numerous diagrams are given illustrating the appearance of the drops under different conditions. The observations are held to support the author's theory of the molecular isomerism of the different modifications of a substance, as opposed to other theories of the relationship between amorphous and crystalline forms. E. H. R.

**Colloidal Phenomena and the Adsorption Formula.** JOHN A. WILSON and WYNNARETTA H. WILSON (*J. Amer. Chem. Soc.*, 1918, **40**, 886—895).—The theory of the mechanism of protein swelling put forward by Procter and Wilson (T., 1916, **109**, 307) is further developed, and the commonly used empirical adsorption formula is discussed in relation to the theory.

It is shown that chemical combination of a colloid jelly with an electrolyte to form an ionised colloid salt will cause the jelly to swell to a maximum, which is followed by a gradually increasing contraction as the concentration of the electrolyte in the solution is increased. If an electrolyte which does not combine with the protein is added to the system, contraction of the swollen jelly takes place to an extent which depends on the resulting ionic concentration.

It is further shown that if the chemically combined electrolyte and the total quantity of electrolyte in the jelly are represented as functions of the concentration of the electrolyte in the external solution, curves are obtained which are of the same form as those which correspond with the empirical adsorption formula.

The microscopic pores found in certain hardened jellies are considered in relation to the continuity of the jellies regarded as two-phase systems. H. M. D.

**Water-in-Oil Emulsions.** ALFRED ULRICH MAX SCHLAEPFER (T., 1918, **113**, 522—526).—With the aid of finely divided carbon as emulsifier, it is possible to make emulsions of water in kerosene, turpentine, benzene, toluene, and other liquids which wet the solid more readily than water does. The results of experiments with varying proportions of kerosene and water are described, and it is shown that the viscosity of the emulsions increases with the amount of water which they contain. In no circumstances was it found possible to obtain emulsions with water as the external phase. The emulsifying action of the carbon depends on the fact that the oil-wetted carbon particles form a skin over the water droplets, and thus prevent their coalescence.

Carron oil is an emulsion of the water-in-oil type, and mixes freely with organic solvents, but not with water without shaking.

H. M. D.

**Equilibrium in the System: Ferrous Carbonate, Carbon Dioxide, and Water.** HERBERT J. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 879—883).—The solubility of ferrous carbonate in aqueous solutions of carbonic acid of varying concentration has been measured at 30°. The experiments were carried out in a steel bottle, which was agitated for several days to ensure the attainment of equilibrium. The ferrous carbonate was prepared by the interaction of equimolecular quantities of ferrous sulphate and sodium hydrogen carbonate at 100° in aqueous solution saturated with carbon dioxide at a pressure of about 30 atmospheres.

The concentrations of the dissolved ferrous salt and carbon dioxide are found to satisfy the relation

$$\alpha[Fe(HCO_3)_2]/\sqrt[3]{[H_2CO_3]}=K,$$

in which $\alpha$ represents the degree of ionisation of the ferrous hydrogen carbonate, which has been assumed to be the same as that of barium nitrate in equivalent concentration. The average value of $K$ is $4{\cdot}04\times10^{-3}$. Since the above theoretical constant $K=\sqrt[3]{K_1K_3/4K_2}$, where $K_1$ and $K_2$ are the first and second ionisation constants for carbonic acid and $K_3$ is the ionic solubility product for ferrous carbonate, it is possible to calculate $K_3$. Putting $K_1=3{\cdot}75\times10^{-7}$ and $K_2=4{\cdot}91\times10^{-11}$, this equation gives $K_3=34{\cdot}53\times10^{-12}$. From this it follows that, in the absence of hydrolytic decomposition, the solubility of ferrous carbonate in pure water would be $5{\cdot}8\times10^{-6}$ gram-molecules per litre.

H. M. D.

**Equilibrium in the System: Zinc Carbonate, Carbon Dioxide, and Water.** HERBERT J. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 883—885).—The experiments were carried out in exactly the same way as those referred to in the preceding abstract. The zinc carbonate was prepared from the purest commercial product, which was treated with successive large quantities of boiling water. The basic carbonate was then subjected to the prolonged action of an aqueous solution of carbon dioxide under a pressure of about 30 atmospheres.

The quantities of zinc carbonate dissolved by carbonic acid solutions of varying concentration at 25° and 30° are in agreement with the formula $a[Zn(HCO_3)_2]/\sqrt{[H_2CO_3]} = 3\cdot36 \times 10^{-3}$, where $a$ is assumed to have the same value as for zinc chloride.

From this value of the equilibrium constant and the ionisation constants for carbonic acid, the ionic solubility product, $K_3 = [Zn^{\cdot\cdot}][CO_3'']$, is found to be $21 \times 10^{-12}$ at 25°. In the absence of hydrolysis, the solubility of zinc carbonate in pure water at 25° would therefore be $4\cdot58 \times 10^{-6}$ gram-molecule per litre.

H. M. D.

**Application of the Mass Law to the Process of Disinfection, being a Contribution to the Mechanistic Theory as Opposed to the Vitalistic Theory.** Richard Edwin Lee and C. A. Gilbert (*J. Physical Chem.*, 1918, **22**, 348—372).—An historical account of the development of the existent theories of disinfection is given, and the various theories, grouped into the two classes vitalistic theories and mechanistic theories, have been subjected to criticism in the light of data accumulated by a number of workers, obtained independently in many places and from some new experimental data of the authors. The velocity of disinfection has been determined in the case of *Bacillus typhosus* with phenol at 37·5°, anthrax spores with mercuric chloride at 20°, and *Staphylococcus pyogenes aureus* with phenol at 20°. In all cases, the disinfectant had a concentration of 0·2%. The velocity of reaction was determined by a modification of the Rideal-Walker drop method. A suitable quantity of the diluted broth culture of the micro-organism under examination was put into a test-tube containing a quantity of disinfectant solution of known concentration, and then placed in an incubator. After successive definite time intervals, accurately measured portions were transferred to Petri dishes and "plated," incubated, and the surviving organisms counted. The authors are of the opinion that the experimental evidence makes it probable that disinfection is an orderly time process which is closely analogous to a chemical reaction, the micro-organisms and the disinfectants being regarded as the respective reagents. A definite logarithmic relationship between velocity of disinfection and concentration has been found to exist in all cases investigated. Confirmation of the foregoing is furnished by the fact that the velocity of disinfection is influenced by variations in temperature and concentration in a manner in accord with the mass law. The explanation why disinfection is not sudden, but takes place according to the mass law, is as follows. Owing to changes in bacterial constituents, only a certain number of individuals are in a condition to be attacked by the disinfectant at a given time, but the total number of individuals in such a condition at any given moment represents a constant proportion of the surviving micro-organisms. The author considers the objections to the mechanistic theory put forward by Reichenbach (*Zeitsch. Hygiene*, 1910, **10**, 237), and points out that it is not necessary to regard disinfection as a reaction of the first order, but rather, as is pointed out by Nernst, as a reaction of a higher order. The theory of graded resistance advanced by Eykman, Hewlett, and Reichel (A., 1909, ii, 1045; *Biochem. Zeitsch.*, 1908, **11**, 12) is criticised, and it is shown that the biological characteristics are distributed as a rule in a manner quite different from that assumed in the formation of the theory. In view of these observations, the authors are led to the conclusion that the logarithmic nature of disinfection is due to a general similarity of the individuals in a given pure culture rather than to a dissimilarity of the individuals as postulated in the theories of graded resistances by the supporters of the vitalistic theory. The authors also point out that although the work of Chick and Martin, and of Browning and Gilmour (*J. Path. and Bact.*, A., 1913, i, 1138), indicates the specificity of disinfectants, this behaviour is to be expected if the disinfection process is analogous to chemical action, for, in the application of the principle of the mass law the influence of the affinity factor is always taken into account. J. F. S.

**Catalysis. IX. Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems.** William Cudmore McCullagh Lewis (T., 1918, **113**, 471—492).—The concept of critical energy and critical increment in connexion with the formation of active molecules is further considered, and it is shown that reaction velocities and equilibrium constants may be calculated on the basis of molecular statistical considerations. Expressions are derived for the velocity of a unimolecular reaction and of bimolecular reactions in which the reacting molecules are of the same kind and also of different kinds. The theoretical treatment includes a consideration of the reaction velocity formulæ in the light of the radiation hypothesis.

The formulæ derived are applied to a number of gaseous reactions which have been experimentally examined, such as the decomposition of hydrogen iodide, the combination of hydrogen and iodine, and the dissociation of iodine, bromine, chlorine, and hydrogen, and it is shown that the calculated results are in fair agreement with those found by experiment. The formulæ may be used for the calculation of velocity or equilibrium constants in regions which do not admit of experimental determination by reason of the extremely high or low velocities which are involved.

The question of the unimolecular decomposition of hydrogen iodide is discussed, and it is shown that the velocity is very small compared with that of the bimolecular change at all temperatures at which this reaction has been examined experimentally. Calculation indicates, however, that the two velocity constants should be of the same order of magnitude in the neighbourhood of 1200° (abs.). At this temperature, the progress of the reaction would consequently not be satisfactorily represented by the equation for a bimolecular change. H. M. D.

**Periodic System of the Elements.** Stefan Meyer (*Physikal. Zeitsch.*, 1918, **19**, 178—179).—The author gives two methods of representing the periodic classification, in the first of which each series is written out at length and arranged in such a way that the eighth group elements lie in the centre of the scheme; to the right the elements of groups 1, 2, 3, etc., in order, and to the left the elements 7, 6, 5, etc. This arrangement places the elements of smallest atomic volume in the centre, so that passing either to the left or right of the centre is accompanied by an increase of atomic volume. In the second arrangement, the alkali metals occupy the middle of the table; to the right the groups follow 2, 3, 4 . . . 8, with + valencies 2—8, and to the left the groups 0, 7, 6 . . . 1, with − valencies 0—7. This arrangement places the elements with largest atomic volume in the centre, and on passing either to the right or left of the centre there is a decrease in atomic volume. The author places both the atomic weights and the atomic numbers alongside the elements. In the first arrangement, the elements of the rare earth group are placed together in groups III and IV to the left of the table, whilst in the second arrangement they are spread out in various groups in the third and fourth long series, although in this case the author definitely states that their positions are not definitely fixed. J. F. S.

**The "De-salting" of Sea-water.** WALTER BRIEGER (*Chem. Zeit.*, 1918, **42**, 302. Compare A., 1911, ii, 723).—Quotations are given from ancient and modern literature to show that sea-water is not freed from salt by passing it through porous earthenware, as stated by Aristotle. W. P. S.

**New Simple Ultra-filters. II. Spontaneous Ultra-filters.** WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1918, **22**, 143—147. Compare this vol., ii, 192).—The efficiency of the ultra-filters which have been previously described has been found to depend on the presence of moisture in the filter paper which is used in the preparation of the filters. Dry filter paper does not give nearly such satisfactory results as filter paper which contains appreciable quantities of moisture. By treatment of moist filter paper with 2% collodion solution in the manner previously described, ultra-filters are obtained which show a markedly increased rapidity of action. Such ultra-filters may be used without the application of external pressure as an aid to filtration. The observed differences in the efficiency of ultra-filters made with dry and moist filter paper are attributable to differences in the structure of the collodion membrane in the two cases. The greatly increased filtering surface which is obtained when moist filter paper is used may be accounted for in terms of the structural peculiarities which are exhibited by the collodion membrane formed at the surface of water.

H. M. D.

**Simplified Short Vacuum Gauge.** ENOCH KARRER (*J. Amer. Chem. Soc.*, 1918, **40**, 928—929).—A modified short Gaede gauge is described in which the connexion between the adjustable mercury receiver and the exhausted space is made through a steel tube which is welded to a tube of platinum foil, which in turn is fused into the lower end of the glass gauge tube. This is silvered and then copper-plated, and the seam in the platinum foil is then rendered gas-tight by a layer of solder bridging the copper-plated glass surface and the surface of the steel tube. H. M. D.

## Inorganic Chemistry.

**Hydrogen Ion Concentrations of Various Indicator End-points in Dilute Sodium Hypochlorite Solutions.** Glenn E. Cullen and J. Harold Austin (*J. Biol. Chem.*, 1918, **34**, 553—568).—The end-points of indicators in dilute sodium hypochlorite solutions are different from the end-points of the same indicators in ordinary solutions, on account of the bleaching action of the hypochlorite. The end-point to powdered phenolphthalein in a 0·5% sodium hypochlorite solution is at a $P_H$ of about 10·1, whilst in an alcoholic solution of *o*-cresolphthalein it is at a $P_H$ of about 9·3. The latter indicator gives an end-point in 1% sodium hypochlorite solution at about $P_H$ 9·6. In the preparation of Dakin's hypochlorite solution (A., 1915, i, 924), the authors recommend that chlorine should be passed into a sodium carbonate solution containing 14 grams to the litre until sodium hypochlorite is formed in a concentration of 0·5%, as shown by titration with thiosulphate. H. W. B.

**Absorption of Atmospheric Gases by Water. II. A Diagram showing the Volume of Oxygen dissolved by Water at Different Temperatures and Pressures. Additions to the Bibliography.** J. H. Coste (*J. Soc. Chem. Ind.*, 1918, **37**, 170—171T. Compare A., 1917, ii, 463).—To facilitate the calculation of the volume of oxygen dissolved in water, the author has constructed a series of graphs which give the number of c.c. of oxygen dissolved in 1 litre of water at temperatures from 0° to 25° and pressures from 710 mm. to 780 mm. An additional bibliography is added to the paper. J. F. S.

**Effect of Acetylene on the Oxidation of Ammonia to Nitric Acid.** Guy B. Taylor and Julian H. Capps (*J. Ind. Eng. Chem.*, 1918, **10**, 457—459).—The presence of a small quantity of acetylene in the ammonia–air mixture has a deleterious effect on the platinum catalyst; with 0·02% of acetylene, the yield falls from 95% to 89% or less, whilst 0·1% of acetylene decreases the yield to 65%. Ammonia gas may be freed from acetylene and other non-reacting gases by dissolving it in water to form a concentrated solution and then vaporising the latter with air. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

**Density, Compressibility, and Atomic Weight of Argon.** A. LEDUC (*Compt. rend.*, 1918, **167**, 70—71).—Working with a carefully purified sample of argon, the author finds for its density the value 1·3787, for its coefficient of departure from Mariotte's law between 1 and 5 atmos., at 14° the value $10 \cdot 2 \times 10^{-6}$, and for its atomic weight the value 39·91. W. G.

**The Reaction between the Alkali Phosphates and Magnesium Chloride.** D. BALAREFF (*Zeitsch. anorg. Chem.*, 1918, **102**, 241—246).—The author has examined the precipitates formed by bringing together under different conditions magnesium chloride and disodium, dipotassium, or dirubidium hydrogen phosphate. Generally, magnesium monohydrogen phosphate is precipitated, with a variable content of water of crystallisation, but it is liable to be contaminated with magnesium monoalkali phosphate, and under suitable conditions the whole of the precipitate may be formed of the latter type of salt. Thus, when a dilute solution of magnesium chloride is added slowly with agitation to a 10% solution of dipotassium hydrogen phosphate, the salt $MgKPO_4,6H_2O$ is precipitated in an almost pure condition, but if the solutions are mixed in the reverse order, the precipitate is of uncertain composition, containing variable quantities of $MgKPO_4$ aq., $MgHPO_4$ aq., $Mg(OH)_2$, and $Mg_3(PO_4)_2$. The rubidium salt, $MgRbPO_4,6H_2O$, can be precipitated almost pure in a similar manner to the potassium salt.

The work of Fröschel has shown (*Ber. Südslav. Akad.*, 1912, **190**, 117—138) that in whatever manner dilute solutions of magnesium chloride and disodium hydrogen phosphate are mixed, equilibrium between the products of reaction is eventually obtained. Fröschel omitted to observe, however, that the precipitate is not pure $MgHPO_4$ aq., but liable to be contaminated with magnesium alkali phosphate. The author quotes analyses showing that when saturated solutions of these salts are mixed, the precipitate contains a considerable quantity of alkali. The results explain the reason for the supposed existence of so many hydrates of $MgHPO_4$, and also emphasise the danger of the presence of alkali cations during the estimation of phosphoric acid by the magnesium ammonium phosphate method. E. H. R.

**Isotopic Lead.** FRANK WIGGLESWORTH CLARKE (*Proc. Nat. Acad. Sci.*, 1918, **4**, 181—188).—The constancy of the atomic weight of lead from non-radioactive minerals and its independence on the species and locality of the mineral suggest that ordinary lead is a distinct variety, not a balanced mixture of the isotopes derived from uranium and thorium. The very variable atomic weight of lead derived from uranium minerals suggests that this "normal" or ordinary lead is present in varying amount along with the isotope derived from uranium. A hypothesis of elementary evolution is suggested, in which ordinary lead is a product of evolution, the lighter elements condensing in the processes into the heavier elements, and the isotopes formed in radioactive change are products of degradation or decay. The atom being a very highly complex structure, in which the constituents must come together in irregular proportions, the process of evolution from the lighter to the heavier forms is regarded as a slow process in which the final stable configuration is not at once attained, but only after a period of selection of the constituent parts. F. S.

**Mercury Hydrosols produced from Metallic Mercury.** IVAR NORDLUND (*Diss.*, *Upsala*, 1918, 1—125).—The preparation of mercury sols has been studied by a variety of methods, which include (*a*) mechanical dispersion methods, (*b*) thermal dispersion methods, and (*c*) electrical dispersion methods. Under the first group of methods, it is shown that by spirting a fine stream of mercury by means of high pressure into solutions of potassium nitrate and gelatin, definite sols of mercury are produced, although the particles are relatively large. With solutions of ammonia, ammonium chloride, ammonium sulphate, or carbamide, or even pure water, no sol-formation occurred by this method. When mercury is shaken with pure water or with dilute solutions of potassium chloride, sodium chloride, potassium nitrate, potassium sulphate, copper sulphate, mercurous nitrate, or acetic acid, there is no formation of colloidal mercury, but if dilute solutions (ca. $10^{-5}N$) of ammonia, ammonium sulphate, ammonium chloride, calcium citrate, tartaric acid, potassium tartrate, carbamide, or gelatin are used, definite colloidal solutions are produced. Mercury sols are also produced by passing hot mercury vapour directly into water. Mercury sols can be readily prepared by the Bredig method of electrical dispersion, using either direct or alternating current. The law of Stokes is tested for the velocity of fall of a mercury drop through an 11% solution of water in glycerol, and the results show that within the limits of experimental error the law holds for this case. The various sols have been examined in connexion with the distribution of the particles. The sols have varying colours from grey to yellowish-brown and reddish-brown; to characterise the colour of the sols more exactly, the absorption spectrum has been determined over the range $\lambda = 253—263\ \mu\mu$. A number of experiments are described on methods of estimating the purity of the sols produced in different ways, the stability toward various electrolytes, and the stabilising action of electrolytes. From kataphoresis experiments, it is shown that the sols are all positively charged except those prepared in citrate and tartrate solutions, which are negatively charged. J. F. S.

**The Chemistry of Quinquevalent Tungsten.** OSCAR O:SON COLLENBURG (*Zeitsch. anorg. Chem.*, 1918, **102**, 247—276).—By the reduction of tungstic acid or a tungstate in oxalic acid solution with tin, the author has succeeded in preparing soluble, fairly stable complex oxalates containing quinquevalent tungsten. These salts have been isolated in a pure condition, and from them other compounds containing quinquevalent tungsten have been prepared. The reduction with tin proceeds smoothly only in the one stage. It is best to reduce a solution of an alkali tungstate in a concentrated solution of oxalic acid containing slight excess of alkali oxalate. The course of the reduction can be followed by the colour change, through dark blue, green, and yellow to deep red. After removal of tin and excess of oxalic acid, the complex oxalate is precipitated by means of alcohol, and can be purified by dissolving in hot water and salting out, the sodium salt with sodium bromide, the potassium salt with potassium iodide. The compounds must be dried in a current of carbon dioxide, but are fairly stable in air when dry. The sodium salt has the composition $3Na_2O,2W_2O_5,4C_2O_3,12H_2O$, and the potassium salt

$$3K_2O,2W_2O_5,4C_2O_3,9H_2O.$$

They are red, crystalline powders which slowly oxidise in air, and at 100° lose their water, but do not decompose. They are very soluble in water, insoluble in organic solvents. Sodium hydroxide in the cold precipitates from their aqueous solution a brown, amorphous substance containing quinquevalent tungsten, but on boiling, part of this dissolves to form a tungstate, whilst a dark residue remains, probably containing quadrivalent tungsten. The complex oxalates can be regarded as *oxalotungstites*, derived from a hypothetical tungstous acid.

The oxalotungstites dissolve in concentrated hydrochloric acid, forming a deep blue solution, which contains an *oxychloride* of quinquevalent tungsten, probably $WOCl_3$. From this solution, complex chlorides can be isolated containing $WOCl_3$ in combination with chlorides of the alkali metals or ammonium or hydrochlorides of organic bases. The ammonium and potassium salts are precipitated by saturating a hydrochloric acid solution of the corresponding oxalotungstite with hydrogen chloride. The rubidium, cæsium, aniline, tetraethyl- and tetrapropyl-ammonium compounds are precipitated when the corresponding chloride is added to a hydrochloric acid solution of an oxalotungstite, and the pyridine and quinoline compounds are prepared by double decomposition of their hydrochlorides with ammonium chlorotungstite. Four types of complex chlorides have been observed. Type *Ia* has the composition $M_2WOCl_5$, in which M may be $NH_4$, Rb, Cs, or $C_6H_5NH_3$; type *Ib*, $M_2WOCl_5,xH_2O$, is represented by the potassium compound; type *IIa*, $MWOCl_4$, is represented by the pyridine and quinoline compounds, and type *IIb*, $MWOCl_4,H_2O$, by tetraethyl- and tetrapropyl-ammonium compounds. The compounds of type I correspond with the so-called molybdenyl chlorides; they form green crystals. Those of type II have no representative among molybdenum compounds; they form shining, brown crystals (*IIa*) or bright, greenish-blue crystals (*IIb*). The latter hold their water with great tenacity, and may be regarded as hydroxy-compounds, for example, $(C_2H_5)_4N,W(OH)_2Cl_4$. The author prefers to regard the compounds as chloro-derivatives of tungstous acid, rather than as double chlorides or tungstyl chlorides, those of type II being derived from *metatungstous acid*, $WO_2,OH$, and those of type I from the hydroxide, $W(OH)_5$.

The *chlorotungstites* are stable in dry air at the ordinary temperature, but decompose with oxidation to tungstates at 60—70°. They are immediately hydrolysed by water with formation of a brown hydroxide, which has not been analysed. The less soluble cæsium compound is, however, far more stable than the readily soluble ammonium and potassium compounds. They dissolve readily in absolute methyl and ethyl alcohols, with the exception of the rubidium and cæsium compounds, but not in other organic solvents. Concentrated hydrochloric acid and 35% sulphuric acid also dissolve them, but alkalis and ammonia decompose them. Oxidising agents convert them into tungstates, and permanganate and iodine have been employed for quantitative determinations of the quinquevalent tungsten.

The chlorotungstites react vigorously with a concentrated solution of potassium cyanide with evolution of hydrogen cyanide. A reddish-yellow solution is formed containing cyanides of the type $M_4W(CN)_8$, from which a sparingly soluble cadmium compound, $Cd_2W(CN)_8,8H_2O$, has been isolated. A thiocyanic acid compound has also been isolated in the form of a pyridine salt having the composition $(PyH)_2WO(SCN)_5,xH_2O$.

Full details for the preparation of each of the chlorotungstites described are given. E. H. R.

**Behaviour of Solutions of Stannic Fluoride.** N. Howell Furman (*J. Amer. Chem. Soc.*, 1918, **40**, 906—914).—Stannic fluoride was prepared by the action of anhydrous hydrogen fluoride on stannic chloride according to the method of Ruff and Plato by the use of apparatus involving a minimum amount of platinum. According to observations on the electrical conductivity of its solutions, it hydrolyses much less rapidly than stannic chloride. The conductivity increases rapidly at first, but attains a constant value after some days. The final value corresponds closely with that calculated on the assumption that complete hydrolysis takes place in accordance with the equation $SnF_4+4H_2O=Sn(OH)_4+4HF$.

Experiments made with a view to ascertain the amount of hydrofluoric acid which is necessary to prevent the precipitation of tin by the action of hydrogen sulphide show that the hydrogen ion concentration must be such that hydrolysis of the stannic fluoride becomes inappreciable. The anomalous behaviour of stannic tin in hydrofluoric acid solution may be explained either by the assumption that stannic fluoride has little tendency to ionise, or by the formation of complex ions of the type $H_nSnF_{4+n}$. Of the two hypotheses, the former seems to be in better agreement with the facts. H. M. D.

**Combinations of Normal Zirconyl Sulphate with some Alkali Sulphates ($K,Na,NH_4$).** Ed. Chauvenet and (Mlle.) H. Gueylard (*Compt. rend.*, 1918, **167**, 24—25. Compare this vol., ammonium heptamolybdate respectively, left for three hours in the dark, and then polarised at about 20° in a 2-dcm. tube. If the molybdate solution becomes green through reduction, a drop of bromine water may be added. J. C. W.

**Estimation of Fatty Acids in Butter Fat.** E. B. HOLLAND and J. P. BUCKLEY, JUN. (*J. Agric. Research*, 1918, **12**, 719—732). —Direct esterification of butter fact (with absolute alcohol containing hydrogen chloride or concentrated sulphuric acid). and subsequent fractional distillation of the resulting esters, affords a trustworthy method for the estimation of certain of the fatty acids. The following quantities of fatty acids were found in butter fat: hexoic acid, 1·36%; octoic acid, 0·975%; decoic acid, 1·831%; lauric acid, 6·895%; myristic acid, 22·618%. Butyric acid (3·153%) and palmitic acid (19·229%) were estimated by difference, stearic acid (11·384%) by crystallisation, and oleic acid (27·374%) from the iodine number of the insoluble fatty acids. [See, further, *J. Soc. Chem. Ind.*, 846A.] W. P. S.

**Test for Acetone in Urine.** M. WAGENAAR (*Pharm. Weekblad*, 1918, **55**, 57—60).—The presence of 0·5 mg. of acetone in 10 c.c. of urine can be detected by mixing the sample with a solution of acetic acid, tartaric acid, and sodium nitroprusside, and covering the liquid with a concentrated solution of ammonia. A coloration like that of permanganate solution is developed at the junction of the liquids. A. J. W.

**Detection of Acetone in Urine.** P. BOHRISCH (*Pharm. Zeit.*, 1918, **63**, 173—174. Compare this vol., ii, 179).—The author finds that Legal's test is more sensitive than Lange's ring test, and mentions that Arends and Urban had shown in 1911 that it was not necessary for the sodium nitroprusside solution used in the tests to be freshly prepared. W. P. S.

**Detection of Arbutin.** HANS SALOMON (*Ber. Deut. pharm. Ges.*, 1918, **28**, 138—139).—The tests commonly applied for arbutin in urine, for example, after the ingestion of bearberry leaf tea, are not specific to this substance. D. F. T.

**Direct Estimation of Urea and Ammonia in Placenta Tissue.** FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1918, **33**, 381—385. Compare Sumner, A., 1916, ii, 655).—The methods of estimation recommended by the author are essentially those devised by Sumner (*loc. cit.*), the chief modification being the addition of potassium carbonate in a solid form to liberate the ammonia prior to aeration. H. W. B.

**Estimation of Uric Acid in Urine and Blood.** D. G. COHEN TERVAERT (*Arch. Néerland. physiol.*, 1918, **2**, 337—345).—In the case of urine, the uric acid is precipitated by ammonium chloride as ammonium urate under conditions described by the author in detail. The precipitate is washed with ammonium chloride by centrifugalisation, then dissolved in lithium carbonate solution, and the uric acid is estimated colorimetrically by Folin's phosphotungstate reagent in a solution made alkaline by sodium carbonate. In the case of blood, the proteins are separated by coagulation of the solution acidified by acetic acid, the filtrate is concentrated to a small bulk, and the uric acid is precipitated as urate and the amount estimated in a manner similar to that described for the estimation of uric acid in urine. S. B. S.

**Estimation of Uric Acid in the Blood by Titration with Permanganate.** J. LUCIEN MORRIS (*Proc. Amer. Soc. Biol. Chem.*, 1917, xxi; *J. Biol. Chem.*, 1918, **33**. Compare A., 1917, ii, 279).—The uric acid from 20 c.c. of blood is isolated as zinc urate. It is then dissolved in hydrochloric acid and disodium hydrogen phosphate added until all the zinc is reprecipitated. A saturated solution of sodium hydrogen carbonate (25 c.c.), 10% potassium iodide (5 c.c.), and 0·5% starch solution (1 c.c.) are added, and 0·002*N*-permanganate run in from a burette until the blue colour of iodide of starch appears. In the slightly alkaline solution, the oxidation of the potassium iodide, and consequent production of the blue iodide of starch, does not occur until all the uric acid has been oxidised. The results are accurate to within 5%. H. W. B.

**Homatropine and the Vitali Test.** H. DROOP RICHMOND (*Analyst*, 1918, **43**, 167—168).—Although the Vitali test serves to distinguish homatropine or its hydrobromide from atropine, hyoscyamine, or hyoscine, it is untrustworthy when applied to homatropine sulphate, since the sulphuric acid in this salt causes the production of a violet coloration. In testing the sulphate, the alkaloid should be isolated and the reaction applied to it instead of to the original salt. W. P. S.

**Microchemical Tests for Choline.** N. SCHOORL (*Pharm. Weekblad*, 1918, **55**, 363—369).—A description of the microchemical characteristics of double salts of choline hydrochloride with platinum chloride, gold chloride, mercuric iodide, bismuth iodide, and of the picrate and picrolonate. A. J. W.

**Estimation of Creatinine and of Creatine in the Blood.** ISIDOR GREENWALD and GRACE MCGUIRE (*J. Biol. Chem.*, 1918, **34**, 103—118).—The new method consists in removing the blood-proteins by heat coagulation in dilute acetic acid solution, and then shaking with kaolin, which almost completely removes the creatinine, leaving the creatine unaffected. After filtration and concentration, the creatine is hydrolysed by hydrochloric acid and estimated by Folin's colorimetric method. H. W. B.

**Detection and Estimation of Quinine in Blood and Urine.** W. RAMSDEN and I. J. LIPKIN (*Ann. Trop. Med. Parasitol*, 1918, **11**, 443—464).—The thalleioquinine reaction is rendered more delicate

(1 : 40,000 with certainty) by adding to 10 c.c. of the quinine solution, feebly acidified with hydrochloric acid and shaken in a test-tube, one-tenth saturated bromine water drop by drop until the pale yellow colour is no longer instantly discharged (white background). At intervals of five seconds, lots of about 2 c.c. are poured into test-tubes containing one drop of concentrated ammonia. Finally, all ammonia solutions are mixed, and the green pigment is extracted with chloroform. The Herapath test may, with Christensen's reagent and a polarising microscope, be employed for the recognition of 1/500 mg. of quinine. Mayer's reaction (ordinarily 1 : 500,000) may be rendered twenty times as delicate by extracting the alkaloid with ether free from all traces of aldehyde or acetone, dissolving in saturated ammonium sulphate solution, and adding 1/100 volume of the reagent. Potassium tri-iodide (limit, 1 : 1,500,000) is less suitable, on account of the colour; phosphotungstic acid and bismuth potassium iodide are much less delicate.

Blood is boiled with ammonium sulphate, urine is precipitated with lead acetate and ammonium sulphate in the presence of acetic acid; in either case, after addition of ammonia to the filtrate, the quinine is extracted with ether free from ketones, the ether is evaporated, and the residue is dissolved in saturated ammonium sulphate solution (at least 10 c.c. for each mg. of quinine). The turbidity due to Mayer's reagent is compared nephelometrically with that in saturated ammonium sulphate solutions containing known amounts of quinine (gauged test-tubes in box with slit for illumination, dark-room, best dilution of quinine 200—300 c.c. per mg.). Thus 0·02—0·03 mg. of quinine in 5 c.c. of blood may be estimated with an error of less than 5%. Larger quantities of quinine (100 mg.) may be precipitated as periodide, from which the quinine is recovered with sodium hydrogen bisulphite and ether, so that it may be weighed or titrated. Gordin's volumetric method (A., 1900, ii, 114, 777; 1907, ii, 487; 1902, ii, 186) is found to be accurate. G. B.

**Detection of Proteins by Bleaching Powder and Hydrochloric Acid.** ADOLF JOLLES (*Deut. med. Woch.*, **43**, 1620—1621; from *Chem. Zentr.*, 1918, i, 303—304).—The test mentioned in the title is not sufficiently sensitive, and can be replaced by the following "three-tube test." The specific reagent contains 10 grams of mercuric chloride, 20 grams of citric acid, and 20 grams of sodium chloride in 500 c.c. of water. To three tubes are added 5 c.c. of filtered urine, to the first tube 1 c.c. of 30% acetic acid + 5 c.c. of the reagent; to the second, 1 c.c. of acetic acid + water, and to the third, water only. All tubes are made to contain the same volume of liquid. By comparing differences in the turbidities after remaining for ten minutes, it is possible to ascertain whether traces of proteins are present. S. B. S.

# General and Physical Chemistry.

**Optics of Disperse Systems. II.** I. Lifschitz and Jens Brandt (*Kolloid Zeitsch.*, 1918, **22**, 133—143. Compare this vol., ii, 181).—The refractive power of disperse systems has been examined by observations on colloidal solutions of sulphur and on soap solutions.

The results obtained with colloidal solutions of sulphur, fractionated by the method described by Odén, show that the refractive index increases with the concentration of the solution (grams per 100 c.c.) according to a linear equation. The density of the sols also increases with the concentration in an approximately linear manner. The value of $(d_s - d_0)/c$, in which $d_s$ is the density of a sol of concentration $c$ and $d_0$ the density of the solvent, is, however, much greater than for solutions of sulphur in carbon disulphide in which the sulphur is present in the molecular condition. The refractivity, measured by Gladstone and Dale's formula, is much more nearly constant than it is when the formula of Lorenz and Lorentz is employed.

The results obtained in measurements of the refractive index of aqueous solutions of sodium oleate, palmitate and stearate, and of potassium palmitate at 70° show that the refractive index changes with the concentration according to a linear formula. The molecular refractivities of the soaps appear to be independent of the concentration, and consequently of the degree of dispersity and of the extent to which the soaps are hydrolysed and dissociated.

H. M. D.

**Effect of an Electric Field on the Spectrum Lines of Helium.** Toshio Takamine and Usaburo Yoshida (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 325—334).—The mode of resolution of the lines λ 5048, λ 5016, λ 4922, λ 4472, λ 4438, λ 4388, and λ 4121 under the influence of electric fields varying in intensity between 3000 and 70,000 volts per cm. is described. With the exception of λ 4686, the resolution of all the helium lines examined has been found to be unsymmetrical with respect to the initial line.

H. M. D.

**Effect of an Electric Field on the Spectrum Lines of Hydrogen. II.** Toshio Takamine and Usaburo Yoshida (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 321—323. Compare A., 1917, ii, 402). —The changes produced by the action of a strong electric field have been examined by the investigation of a further series of hydrogen lines. The photographs show that the outer components of the lines belonging to the Balmer series frequently extend into the region of the unaffected secondary lines. The apparent lack of any connexion between the two groups of lines suggests that they are due to different carriers. H. M. D.

**Effect of an Electric Field on the Spectrum Lines of Hydrogen.** SHIGEHARU NITTA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 349—355. Compare preceding abstract).—The Stark effect has been examined with electric fields of considerably greater intensity than those used by previous observers. The $H_\beta$ line yields six components, the separation of which is proportional to the intensity of the field. In addition to the Balmer lines, certain lines belonging to the secondary spectrum were investigated. H. M. D.

**Optical Investigations on the Constitution of the Nitrates.** KONR. SCHAEFER (*Zeitsch. wiss. Photochem.*, 1918, **17**, 193—217. Compare A., 1910, ii, 562; 1917, ii, 61, 186).—The ultra-violet absorption of aqueous solutions of various nitrates has been examined over a considerable range of concentration. The results obtained for glucinum, silver, thallous, copper, mercurous, cerous, bismuth, and thorium nitrate are shown in the form of logarithmic absorption curves. On examining the available data for the nitrates, it would seem that these may be divided into three groups according to their optical behaviour at different concentrations. The nitrates of the alkali and alkaline earth metals satisfy the requirements of Beer's law. This relation is only approximately satisfied by the nitrates of glucinum, magnesium, aluminium, manganese, zinc, cadmium, lead, cobalt, and nickel, which form the second group. The deviations are partly due to hydrolysis and in part to the superposed absorption effect of the metal. To the third group belong the nitrates of metals which show large divergences from Beer's law. The absorption of the nitrates in this group (copper, silver, thallous, mercurous) increases rapidly with increase in the concentration of the solutions. This grouping of the metallic nitrates shows an undoubted connexion between the optical properties and the electro-affinity of the metals. The nitrates of the strongly electropositive metals show the selective absorption which has been attributed to that arrangement of the atoms which is found in the nitrate ion, as distinguished from the non-selective absorption of the grouping which is characteristic of the organic nitrates and of concentrated nitric acid. The absorption exhibited by the nitrates of the weak electropositive metals cannot be satisfactorily explained in terms of these two forms of the nitrate group, and it is suggested that the optical behaviour affords evidence of a third configuration of the atoms in the nitrate group.

The absorption of fused potassium nitrate has also been examined, and the selective absorption which it exhibits resembles closely that found for aqueous solutions of the alkali nitrates. In this respect it differs markedly from the absorption of anhydrous nitric acid, which shows no selective effect, although this is shown by dilute aqueous solutions of the acid. H. M. D.

**Spectral Reaction of Methylfurfuraldehyde and β-Hydroxy-δ-methylfurfuraldehyde.** (KINTARŌ OSHIMA and TETSUTARŌ TADOKORO (*J. Tokyo Chem. Soc.*, 1918, **39**, 23—30. Compare Oshima and Tollens, A., 1901, ii, 484).—A comparison of the absorption spectrum of samples of hydroxymethylfurfuraldehyde (as phloroglucide in hydrochloric acid solution) from various sources shows identity of the substance prepared by Kiermayer's method with that obtained from dextrose, lævulose, or inulin by distillation with hydrochloric acid. With hydroxymethylfurfuraldehyde prepared from galactose and lactose, the absorption band is shifted a little towards the F-line, and even slightly overlaps that line in the case of samples prepared from sucrose. These different absorption spectra can, however, be readily distinguished from that given by methylfurfuraldehyde. S. H.

**The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. The Influence of certain Inorganic Haloids on the Optical Rotatory Powers of α-Hydroxy-acids, α-Amino-acids, and their Derivatives.** GEORGE WILLIAM CLOUGH (T., 1918, **113**, 526—554).—The author has compared the effect of sodium haloid salts on the optical rotatory powers of *l*-lactic, *d*-glyceric, *l*-malic, and *d*-tartaric acids and certain of their esters, and the effect of introducing a given radicle into the molecules of the configuratively similar hydroxy-acids, *l*-lactic, *l*-glyceric, *d*-malic, and *d*-tartaric acids, and from his results assumes that the optical rotatory powers of similarly constituted compounds possessing the same configuration are in general influenced similarly by the same changes in the external conditions and also by the introduction of the same substituent into a given radicle attached to the asymmetric carbon atom. The rotatory powers of the above four acids and of *d*-α-hydroxybutyric, *l*-α-hydroxy*iso*valeric, *d*-α-hydroxy*iso*hexoic, *d*-α-hydroxy-β-phenylpropionic, and *d*-α-hydroxyglutaric acids and their derivatives indicate that all these acids possess the same relative configurations, and they are designed as "*d*"-acids. Of the naturally occurring α-amino-acids, it is similarly assumed that *d*-alanine, *l*-serine, *l*-aspartic acid, *d*-valine, *l*-leucine, *d*-*iso*leucine, *d*-α-aminobutyric acid, *d*-glutamic acid, *l*-phenylalanine, and *l*-tyrosine all possess the same configurations, denoted by the symbol "*l*." The dextrorotatory (*d*-) α-halogen acids which have been isolated are assumed to be configuratively similar compounds and related configuratively to the "*l*"-amino-acids, which it is suggested are enantiomorphously related to the "*d*"-hydroxy-acids. This is supported by a comparison of the rotatory powers of the optically active α-bromoacylamino-acids with those of the α-aminoacylamino-acids. W. G.

**The Radioactivity of the Waters of Neuchâtel and Seeland.** H. PERRET and A. JAQUEROD (*Arch. Sci. phys. nat.*, 1918, [iv], **45**, 277—297, 336—348, 418—437).—The content in radium emanation of the spring waters in a very small region, the Neuchâtel Jura mountains and neighbourhood, has been exhaustively studied. Then a minute parallel study of two regions, each of only a few square kilometres, and, lastly, the prolonged parallel study of two springs in the same district and then in different districts, were carried out. More than a hundred springs were examined. The radioactivity of these springs is feeble and varies between 0 and $3{\cdot}5 \times 10^{-10}$ curie of emanation per litre, the quantity varying in all the springs considerably with the time. No relation was found between radioactivity and the volume of flow of the spring or its temperature, and the few thermal and mineral springs found were not especially radioactive. In passing across the Jura chain from S.E. to N.W., there is a marked increase in the radioactivity of the water. The crystalline rocks beneath come nearer to the surface in travelling in this direction. The two springs examined continuously showed maxima and minima of radioactivity recurring at the same intervals of time. The quantity of radioactive salts in the waters was too small to be detected. F. S.

**Sign of the Zinc Electrode.** WILDER D. BANCROFT (*J. Physical Chem.*, 1918, **22**, 371—379).—A theoretical paper in which the sign given to potential values is discussed. It is pointed out that with electrodes which form cations, the *E.M.F.* is a measure of the difference of the chemical potentials, but has the opposite sign; with electrodes which form anions, the two potentials have the same sign. Since the electrical potential of the copper in a Daniell cell is higher than that of the zinc, and since the zinc electrode is the place of lowest electrical potential, although highest chemical potential, it follows that the minus sign ought to be used when writing the potential difference $Zn|ZnSO_4$. This is in keeping with the practice of physicists and physical chemists.

J. F. S.

**Photochemical Cell, containing Complex Cyanides of Nickel or Platinum.** SATOYASU IIMORI (*J. Tokyo Chem. Soc.*, 1918, **39**, 1—13).—A photochemical cell was constructed with platinum electrodes, which were immersed in a solution of potassium nickel cyanide or potassium platinocyanide, one only of the electrodes being exposed to light. In this cell the electrode exposed to light is positive, but in a photochemical cell containing a solution of potassium ferrocyanide, previously described by the author (*ibid.*, 1917, **38**, 507), it was negative. The current from the present cell decays rapidly when the circuit is closed, notwithstanding the insertion of a considerable resistance, but in the former cell a constant current was obtained during the exposure to light. The cause of the *E.M.F.* of this cell is not yet known with certainty, but it would seem not to be the photoelectrical effect on the electrode, as it is not observed when the complex cyanides are replaced by other salt solutions. S. H.

**Method for Determining the Temperature of Luminous Flames.** HERMANN SENFTLEBEN and ELISABETH BENEDICT (*Physikal. Zeitsch.*, 1918, **19**, 180—181).—The temperature of luminous flames is obtained by inserting thin platinum or gold wires into the flame and estimating the temperature of the wires by means of a Holborn-Kurlbaum pyrometer. To compensate for the loss of temperature occasioned by the insertion of the wire, it is raised to the temperature of the flame by the passage of an electric current. When the wire and flame are exactly at the same temperature there is no deposition of carbon, but if the temperature of the wire is lowered slightly there is an immediate deposition of carbon. To correct, if necessary, for the change of temperature brought about by change in the shape of the flame owing to the insertion of the wire, measurements were made with wire of varying diameters (0·2—1·0 mm.), and it was shown that only at greater diameters than these does the temperature depend on the thickness of the wire. The temperature of the middle of a Hefner lamp flame determined by this method is found to be 1690° abs., which is about the mean of the previously recorded values (1680—1711°). J. F. S.

**Improved Form of Thermo-regulator.** JOHN B. FERGUSON (*J. Amer. Chem. Soc.*, 1918, **40**, 929—930).—The adjustment of the level of the mercury in the regulator tube is made by means of a plunger, and the mercury makes contact with a fixed platinum wire. H. M. D.

**Thermo-regulator for Apparatus fitted with a Constant Water-level.** JAROSLAV MILBAUER (*Zeitsch. anal. Chem.*, 1918, **57**, 162—164).—The overflow water from the apparatus is conducted into one limb of a U-tube, the lower part of which is constricted and filled with mercury; the excess of water leaves the upper end of the limb of the U-tube through a side tube, a small by-pass being also fitted at the lower part of the limb. The other limb contains a floating valve, the lower end of which rests on the surface of the mercury. Should the supply of water be interrupted, the limb of the U-tube empties through the by-pass, decreasing the pressure on the mercury, and the valve falls, thus cutting off the supply of gas to the burner under the apparatus.

W. P. S.

**Cineole as a Solvent in Cryoscopy.** CHARLES E. FAWSITT and CHRISTAIN H. FISCHER (*J. Roy. Soc. New South Wales*, 1918, **51**, 467—472).—Cineole is an oil of the formula $C_{10}H_{18}O$ which occurs largely in oil of eucalyptus. It is extracted by simple freezing. This substance has b. p. 175—176°, m. p. 0·9°, it is very hygroscopic, and the presence of water in the product accounts for the m. p. $-1°$ usually given. Cineole is not generally useful as a cryoscopic solvent, chiefly on account of its hygroscopic properties, but in some cases it is found to be a more suitable solvent than benzene, although somewhat more difficult to work with. It has a cryoscopic constant 6·7 and a latent heat of fusion 22·2 cal. per gram. J. F. S.

**The Saturated Vapour Processes of Penta-atomic Substances.** E. ARIÈS (*Compt. rend.*, 1918, **166**, 935—939).—Taking Young's values for the physical constants of stannic chloride, the author deduces the formula $\Pi = \tau^{20/7}Z/x$, where

$$x = \{1 + (1-\tau)(0{\cdot}84-\tau)/[1{\cdot}8(1-\tau)^2 + 0{\cdot}9]\}\tau^{13/7}$$

for the saturated vapour pressures of penta-atomic substances. The values calculated from this formula for methyl fluoride are in fairly close accord with those observed by Collie, except at a temperature of −5°. There is not such close agreement in the case of chloroform with the values as obtained by Regnault unless the critical constants of chloroform are taken as 247° and 45·26 atmos.

W. G.

**Rapid Pressure Method for the Determination of Molecular Weights and Hydrogen Equivalents.** W. H. CHAPIN (*J. Physical Chem.*, 1918, **22**, 337—344).—A modification of the vapour density method of determining molecular weights by measuring the pressure set up by a known weight of vapour in a known volume at a measured temperature. The apparatus used consists of a 500 c.c. distilling flask the side tube of which is replaced by a mercury manometer. The manometer tube is 5 mm. diameter and 20 cm. high, and is fitted with a sliding celluloid scale. The top of the flask is fitted with the usual device for dropping in the substance at the right moment. The method is available for all liquids boiling below 90°. The substance is volatilised by steam, and as the whole of the apparatus is not at a uniform temperature, the average temperature must be computed. A method for deducing the average temperature is indicated. The usual precautions are taken in making the pressure measurement. An interesting innovation is introduced in the use of gelatin capsules for weighing the substance under investigation.

The same apparatus can be used for the determination of the equivalents of the metals zinc, aluminium, sodium, calcium, and magnesium. In all cases except sodium, weighed quantities of the metals are dropped into a measured volume of *N*—3*N*-hydrochloric acid contained in the bulb of the apparatus; with sodium, alcohol is used.

J. F. S.

**Heat of Formation of the Anhydrous Calcium Borates.** R. GRIVEAU (*Compt. rend.*, 1918, **166**, 993—995).—The pure anhydrous calcium borates were prepared by adding the calculated quantity of calcium carbonate to fused boric anhydride. The heat of solution of each of these borates in *N*/2-hydrochloric acid was then determined, and from these results the heat of formation of each borate was calculated, the results obtained being given by the equation:

$2B_2O_3$ sol. + CaO sol. = $2B_2O_3$,CaO sol. + 39·8 cal.
$B_2O_3$ sol. + CaO sol. = $B_2O_3$,CaO sol. + 30·9 cal.
$B_2O_3$ sol. + 2CaO sol. = $B_2O_3$,2CaO sol. + 48·5 cal.
$B_2O_3$ sol. + 3CaO sol. = $B_2O_3$,3CaO sol. + 62·2 cal.

The energy of combination of each successive molecule of calcium oxide with two molecules of boric anhydride diminishes from 39·8 cal. to 13·7 cal.
W. G.

**Apparatus for Cleansing Pyknometers.** MARCEL DUGARDIN (*Ann. Chim. anal.*, 1918, **23**, 125—126).—A narrow glass tube, connected with a flask and a water-pump, is passed down the neck of the pyknometer so that the contents of the latter may be drawn off; water is then admitted to the pyknometer and drawn off again by means of the narrow tube.
W. P. S.

**Adsorption Compounds.** R. HALLER (*Kolloid Zeitsch.*, 1918, **22**, 113—133).—The formation of adsorption compounds by the interaction of dyes with other substances has been examined. Towards chemically indifferent solvents, adsorption compounds behave like mechanical mixtures. Adsorption compounds with a colourless adsorbent when dissolved in a suitable solvent show the same absorption spectrum as the corresponding solution of the dye. The melting points of adsorption compounds containing an adsorbent of low melting point are not very different from the melting point of the adsorbent. The general physical behaviour of the so-called adsorption compounds leads, therefore, to the conclusion that these are to be regarded as mechanical mixtures. [Compare *J. Soc. Chem. Ind.*, 411A.]
H. M. D.

**Certain Relations between Crystalline Form, Chemical Constitution, and Optical Properties in Organic Compounds.** EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1918, **8**, 277—285, 319—327).—In the expectation that there should be discoverable some relationship between the optical and the geometrical constants of crystals, an investigation has been made of a number of organic substances typical of the different classes of the tetragonal system. Making use of the Lorentz-Lorenz expression $(n^2-1)/(n^2+2)$, the author calculates refractivity constants $R_\omega$ and $R_\epsilon$ for the two principal refractive indices $\omega$ and $\epsilon$, and finds that, in a number of cases, the ratio of these constants is almost exactly equal to the reciprocal of the crystallographic axial ratio in the corresponding directions in the crystal structure. Thus in the case of carbamide (tetragonal scalenohedral), $R_\omega/R_\epsilon = 0{\cdot}834$, $a:c = 0{\cdot}833$; in pentaerythritol (ditetragonal pyramidal), $R_3/R_\epsilon = 1{\cdot}07$, $a:c=1{\cdot}024$; and in mellite, $C_6(CO_2)_6Al_2,18H_2O$ (ditetragonal bipyramidal), $R_\omega/R_\epsilon = 1{\cdot}046$, $a:c=1{\cdot}055$. A similar relation holds in the double propionates of calcium with strontium and lead, and in isomorphous mixtures of the latter with the corresponding cubic calcium–barium double salt. It is pointed out that the refraction ratios, as well as the crystallographic axial ratios, are connected with the spacing of the planes of atoms in the space-lattices of the substances, and that comparison of the two ratios may be expected to throw light on the type of space-lattice represented in each case. Skeleton space-lattices are suggested for the above-mentioned substances. A number of exceptions to the rule of inverse proportionality occur. In some cases the deviation is due to an incorrect choice of axial ratios; in others it may be attributed to the presence of asymmetric carbon atoms or to atomic anisotropism. E. H. R.

**Liquid Crystals of the Hydrates of 10-Bromophenanthrene-3- or -6-Sulphonic Acid.** O. LEHMANN (*Ann. Physik.*, 1918, [iv], **55**, 81—102).—In the solid state, the compound forms thin leaflets belonging apparently to the rhombic system, only slightly soluble in hydrochloric acid, from which it was recrystallised, easily soluble in alcohol, but with decomposition and separation of slender needles. The compound forms two liquid crystalline hydrates with water, the one with little water being slimy or gelatinous, that with more water forming separate liquid crystalline drops. The two forms appear to form mixed crystals to a limited extent. The liquid drops have been examined microscopically in great detail, both with ordinary and polarised light, and numerous diagrams are given illustrating the appearance of the drops under different conditions. The observations are held to support the author's theory of the molecular isomerism of the different modifications of a substance, as opposed to other theories of the relationship between amorphous and crystalline forms. E. H. R.

**Colloidal Phenomena and the Adsorption Formula.** JOHN A. WILSON and WYNNARETTA H. WILSON (*J. Amer. Chem. Soc.*, 1918, **40**, 886—895).—The theory of the mechanism of protein swelling put forward by Procter and Wilson (T., 1916, **109**, 307) is further developed, and the commonly used empirical adsorption formula is discussed in relation to the theory.

It is shown that chemical combination of a colloid jelly with an electrolyte to form an ionised colloid salt will cause the jelly to swell to a maximum, which is followed by a gradually increasing contraction as the concentration of the electrolyte in the solution is increased. If an electrolyte which does not combine with the protein is added to the system, contraction of the swollen jelly takes place to an extent which depends on the resulting ionic concentration.

It is further shown that if the chemically combined electrolyte and the total quantity of electrolyte in the jelly are represented as functions of the concentration of the electrolyte in the external solution, curves are obtained which are of the same form as those which correspond with the empirical adsorption formula.

The microscopic pores found in certain hardened jellies are considered in relation to the continuity of the jellies regarded as two-phase systems. H. M. D.

**Water-in-Oil Emulsions.** ALFRED ULRICH MAX SCHLAEPFER (T., 1918, **113**, 522—526).—With the aid of finely divided carbon as emulsifier, it is possible to make emulsions of water in kerosene, turpentine, benzene, toluene, and other liquids which wet the solid more readily than water does. The results of experiments with varying proportions of kerosene and water are described, and it is shown that the viscosity of the emulsions increases with the amount of water which they contain. In no circumstances was it found possible to obtain emulsions with water as the external phase. The emulsifying action of the carbon depends on the fact that the oil-wetted carbon particles form a skin over the water droplets, and thus prevent their coalescence.

Carron oil is an emulsion of the water-in-oil type, and mixes freely with organic solvents, but not with water without shaking.

H. M. D.

**Equilibrium in the System: Ferrous Carbonate, Carbon Dioxide, and Water.** HERBERT J. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 879—883).—The solubility of ferrous carbonate in aqueous solutions of carbonic acid of varying concentration has been measured at 30°. The experiments were carried out in a steel bottle, which was agitated for several days to ensure the attainment of equilibrium. The ferrous carbonate was prepared by the interaction of equimolecular quantities of ferrous sulphate and sodium hydrogen carbonate at 100° in aqueous solution saturated with carbon dioxide at a pressure of about 30 atmospheres.

The concentrations of the dissolved ferrous salt and carbon dioxide are found to satisfy the relation

$$\alpha[Fe(HCO_3)_2]/\sqrt[3]{[H_2CO_3]}=K,$$

in which $\alpha$ represents the degree of ionisation of the ferrous hydrogen carbonate, which has been assumed to be the same as that of barium nitrate in equivalent concentration. The average value of $K$ is $4{\cdot}04\times10^{-3}$. Since the above theoretical constant $K=\sqrt[3]{K_1K_3/4K_2}$, where $K_1$ and $K_2$ are the first and second ionisation constants for carbonic acid and $K_3$ is the ionic solubility product for ferrous carbonate, it is possible to calculate $K_3$. Putting $K_1=3{\cdot}75\times10^{-7}$ and $K_2=4{\cdot}91\times10^{-11}$, this equation gives $K_3=34{\cdot}53\times10^{-12}$. From this it follows that, in the absence of hydrolytic decomposition, the solubility of ferrous carbonate in pure water would be $5{\cdot}8\times10^{-6}$ gram-molecules per litre.

H. M. D.

**Equilibrium in the System: Zinc Carbonate, Carbon Dioxide, and Water.** HERBERT J. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 883—885).—The experiments were carried out in exactly the same way as those referred to in the preceding abstract. The zinc carbonate was prepared from the purest commercial product, which was treated with successive large quantities of boiling water. The basic carbonate was then subjected to the prolonged action of an aqueous solution of carbon dioxide under a pressure of about 30 atmospheres.

The quantities of zinc carbonate dissolved by carbonic acid solutions of varying concentration at 25° and 30° are in agreement with the formula $\alpha[Zn(HCO_3)_2]/\sqrt{[H_2CO_3]}=3{\cdot}36\times10^{-3}$, where $\alpha$ is assumed to have the same value as for zinc chloride.

From this value of the equilibrium constant and the ionisation constants for carbonic acid, the ionic solubility product, $K_3=[Zn^{\cdot\cdot}][CO_3'']$, is found to be $21\times10^{-12}$ at 25°. In the absence of hydrolysis, the solubility of zinc carbonate in pure water at 25° would therefore be $4{\cdot}58\times10^{-6}$ gram-molecule per litre.

H. M. D.

**Application of the Mass Law to the Process of Disinfection, being a Contribution to the Mechanistic Theory as Opposed to the Vitalistic Theory.** Richard Edwin Lee and C. A. Gilbert (*J. Physical Chem.*, 1918, **22**, 348—372).—An historical account of the development of the existent theories of disinfection is given, and the various theories, grouped into the two classes vitalistic theories and mechanistic theories, have been subjected to criticism in the light of data accumulated by a number of workers, obtained independently in many places and from some new experimental data of the authors. The velocity of disinfection has been determined in the case of *Bacillus typhosus* with phenol at 37·5°, anthrax spores with mercuric chloride at 20°, and *Staphylococcus pyogenes aureus* with phenol at 20°. In all cases, the disinfectant had a concentration of 0·2%. The velocity of reaction was determined by a modification of the Rideal-Walker drop method. A suitable quantity of the diluted broth culture of the micro-organism under examination was put into a test-tube containing a quantity of disinfectant solution of known concentration, and then placed in an incubator. After successive definite time intervals, accurately measured portions were transferred to Petri dishes and "plated," incubated, and the surviving organisms counted. The authors are of the opinion that the experimental evidence makes it probable that disinfection is an orderly time process which is closely analogous to a chemical reaction, the micro-organisms and the disinfectants being regarded as the respective reagents. A definite logarithmic relationship between velocity of disinfection and concentration has been found to exist in all cases investigated. Confirmation of the foregoing is furnished by the fact that the velocity of disinfection is influenced by variations in temperature and concentration in a manner in accord with the mass law. The explanation why disinfection is not sudden, but takes place according to the mass law, is as follows. Owing to changes in bacterial constituents, only a certain number of individuals are in a condition to be attacked by the disinfectant at a given time, but the total number of individuals in such a condition at any given moment represents a constant proportion of the surviving micro-organisms. The author considers the objections to the mechanistic theory put forward by Reichenbach (*Zeitsch. Hygiene*, 1910, **10**, 237), and points out that it is not necessary to regard disinfection as a reaction of the first order, but rather, as is pointed out by Nernst, as a reaction of a higher order. The theory of graded resistance advanced by Eykman, Hewlett, and Reichel (A., 1909, ii, 1045; *Biochem. Zeitsch.*, 1908, **11**, 12) is criticised, and it is shown that the biological characteristics are distributed as a rule in a manner quite different from that assumed in the formation of the theory. In view of these observations, the authors are led to the conclusion that the logarithmic nature of disinfection is due to a general similarity of the individuals in a given pure culture rather than to a dissimilarity of the individuals as postulated in the theories of graded resistances by the supporters of the vitalistic theory. The authors also point out that although the work of Chick and Martin, and of Browning and Gilmour (*J. Path and Bact.*, A., 1913, i, 1138), indicates the specificity of disinfectants, this behaviour is to be expected if the disinfection process is analogous to chemical action, for in the application of the principle of the mass law the influence of the affinity factor is always taken into account. J. F. S.

**Catalysis. IX. Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems.** William Cudmore McCullagh Lewis (T., 1918, **113**, 471—492).—The concept of critical energy and critical increment in connexion with the formation of active molecules is further considered, and it is shown that reaction velocities and equilibrium constants may be calculated on the basis of molecular statistical considerations. Expressions are derived for the velocity of a unimolecular reaction and of bimolecular reactions in which the reacting molecules are of the same kind and also of different kinds. The theoretical treatment includes a consideration of the reaction velocity formulæ in the light of the radiation hypothesis.

The formulæ derived are applied to a number of gaseous reactions which have been experimentally examined, such as the decomposition of hydrogen iodide, the combination of hydrogen and iodine, and the dissociation of iodine, bromine, chlorine, and hydrogen, and it is shown that the calculated results are in fair agreement with those found by experiment. The formulæ may be used for the calculation of velocity or equilibrium constants in regions which do not admit of experimental determination by reason of the extremely high or low velocities which are involved.

The question of the unimolecular decomposition of hydrogen iodide is discussed, and it is shown that the velocity is very small compared with that of the bimolecular change at all temperatures at which this reaction has been examined experimentally. Calculation indicates, however, that the two velocity constants should be of the same order of magnitude in the neighbourhood of 1200° (abs.). At this temperature, the progress of the reaction would consequently not be satisfactorily represented by the equation for a bimolecular change. H. M. D.

**Periodic System of the Elements.** Stefan Meyer (*Physikal. Zeitsch.*, 1918, **19**, 178—179).—The author gives two methods of representing the periodic classification, in the first of which each series is written out at length and arranged in such a way that the eighth group elements lie in the centre of the scheme; to the right the elements of groups 1, 2, 3, etc., in order, and to the left the elements 7, 6, 5, etc. This arrangement places the elements of smallest atomic volume in the centre, so that passing either to the left or right of the centre is accompanied by an increase of atomic volume. In the second arrangement, the alkali metals occupy the middle of the table; to the right the groups follow 2, 3, 4 . . . 8, with + valencies 2—8, and to the left the groups 0, 7, 6 . . . 1, with − valencies 0—7. This arrangement places the elements with largest atomic volume in the centre, and on passing either to the right or left of the centre there is a decrease in atomic volume. The author places both the atomic weights and the atomic numbers alongside the elements. In the first arrangement, the elements of the rare earth group are placed together in groups III and IV to the left of the table, whilst in the second arrangement they are spread out in various groups in the third and fourth long series, although in this case the author definitely states that their positions are not definitely fixed. J. F. S.

**The "De-salting" of Sea-water.** WALTER BRIEGER (*Chem. Zeit.*, 1918, **42**, 302. Compare A., 1911, ii, 723).—Quotations are given from ancient and modern literature to show that sea-water is not freed from salt by passing it through porous earthenware, as stated by Aristotle. W. P. S.

**New Simple Ultra-filters. II. Spontaneous Ultra-filters.** WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1918, **22**, 143—147. Compare this vol., ii, 192).—The efficiency of the ultra-filters which have been previously described has been found to depend on the presence of moisture in the filter paper which is used in the preparation of the filters. Dry filter paper does not give nearly such satisfactory results as filter paper which contains appreciable quantities of moisture. By treatment of moist filter paper with 2% collodion solution in the manner previously described, ultra-filters are obtained which show a markedly increased rapidity of action. Such ultra-filters may be used without the application of external pressure as an aid to filtration. The observed differences in the efficiency of ultra-filters made with dry and moist filter paper are attributable to differences in the structure of the collodion membrane in the two cases. The greatly increased filtering surface which is obtained when moist filter paper is used may be accounted for in terms of the structural peculiarities which are exhibited by the collodion membrane formed at the surface of water.

H. M. D.

**Simplified Short Vacuum Gauge.** ENOCH KARRER (*J. Amer. Chem. Soc.*, 1918, **40**, 928—929).—A modified short Gaede gauge is described in which the connexion between the adjustable mercury receiver and the exhausted space is made through a steel tube which is welded to a tube of platinum foil, which in turn is fused into the lower end of the glass gauge tube. This is silvered and then copper-plated, and the seam in the platinum foil is then rendered gas-tight by a layer of solder bridging the copper-plated glass surface and the surface of the steel tube. H. M. D.

# Inorganic Chemistry.

**Hydrogen Ion Concentrations of Various Indicator End-points in Dilute Sodium Hypochlorite Solutions.** GLENN E. CULLEN and J. HAROLD AUSTIN (*J. Biol. Chem.*, 1918, **34**, 553—568).—The end-points of indicators in dilute sodium hypochlorite solutions are different from the end-points of the same indicators in ordinary solutions, on account of the bleaching action of the hypochlorite. The end-point to powdered phenolphthalein in a 0·5% sodium hypochlorite solution is at a $P_H$ of about 10·1, whilst in an alcoholic solution of *o*-cresolphthalein it is at a $P_H$ of about 9·3. The latter indicator gives an end-point in 1% sodium hypochlorite solution at about $P_H$ 9·6. In the preparation of Dakin's hypochlorite solution (A., 1915, i, 924), the authors recommend that chlorine should be passed into a sodium carbonate solution containing 14 grams to the litre until sodium hypochlorite is formed in a concentration of 0·5%, as shown by titration with thiosulphate. H. W. B.

**Absorption of Atmospheric Gases by Water. II. A Diagram showing the Volume of Oxygen dissolved by Water at Different Temperatures and Pressures. Additions to the Bibliography.** J. H. COSTE (*J. Soc. Chem. Ind.*, 1918, **37**, 170—171T. Compare A., 1917, ii, 463).—To facilitate the calculation of the volume of oxygen dissolved in water, the author has constructed a series of graphs which give the number of c.c. of oxygen dissolved in 1 litre of water at temperatures from 0° to 25° and pressures from 710 mm. to 780 mm. An additional bibliography is added to the paper. J. F. S.

**Effect of Acetylene on the Oxidation of Ammonia to Nitric Acid.** GUY B. TAYLOR and JULIAN H. CAPPS (*J. Ind. Eng. Chem.*, 1918, **10**, 457—459).—The presence of a small quantity of acetylene in the ammonia–air mixture has a deleterious effect on the platinum catalyst; with 0·02% of acetylene, the yield falls from 95% to 89% or less, whilst 0·1% of acetylene decreases the yield to 65%. Ammonia gas may be freed from acetylene and other non-reacting gases by dissolving it in water to form a concentrated solution and then vaporising the latter with air. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

**Density, Compressibility, and Atomic Weight of Argon.** A. Leduc (*Compt. rend.*, 1918, **167**, 70—71).—Working with a carefully purified sample of argon, the author finds for its density the value 1·3787, for its coefficient of departure from Mariotte's law between 1 and 5 atmos., at 14° the value $10·2 \times 10^{-6}$, and for its atomic weight the value 39·91. W. G.

**The Reaction between the Alkali Phosphates and Magnesium Chloride.** D. Balareff (*Zeitsch. anorg. Chem.*, 1918, **102**, 241—246).—The author has examined the precipitates formed by bringing together under different conditions magnesium chloride and disodium, dipotassium, or dirubidium hydrogen phosphate. Generally, magnesium monohydrogen phosphate is precipitated, with a variable content of water of crystallisation, but it is liable to be contaminated with magnesium monoalkali phosphate, and under suitable conditions the whole of the precipitate may be formed of the latter type of salt. Thus, when a dilute solution of magnesium chloride is added slowly with agitation to a 10% solution of dipotassium hydrogen phosphate, the salt $MgKPO_4,6H_2O$ is precipitated in an almost pure condition, but if the solutions are mixed in the reverse order, the precipitate is of uncertain composition, containing variable quantities of $MgKPO_4$ aq., $MgHPO_4$ aq., $Mg(OH)_2$, and $Mg_3(PO_4)_2$. The rubidium salt, $MgRbPO_4,6H_2O$, can be precipitated almost pure in a similar manner to the potassium salt.

The work of Fröschel has shown (*Ber. Südslav. Akad.*, 1912, **190**, 117—138) that in whatever manner dilute solutions of magnesium chloride and disodium hydrogen phosphate are mixed, equilibrium between the products of reaction is eventually obtained. Fröschel omitted to observe, however, that the precipitate is not pure $MgHPO_4$ aq., but liable to be contaminated with magnesium alkali phosphate. The author quotes analyses showing that when saturated solutions of these salts are mixed, the precipitate contains a considerable quantity of alkali. The results explain the reason for the supposed existence of so many hydrates of $MgHPO_4$, and also emphasise the danger of the presence of alkali cations during the estimation of phosphoric acid by the magnesium ammonium phosphate method. E. H. R.

**Isotopic Lead.** Frank Wigglesworth Clarke (*Proc. Nat. Acad. Sci.*, 1918, **4**, 181—188).—The constancy of the atomic weight of lead from non-radioactive minerals and its independence on the species and locality of the mineral suggest that ordinary lead is a distinct variety, not a balanced mixture of the isotopes derived from uranium and thorium. The very variable atomic weight of lead derived from uranium minerals suggests that this "normal" or ordinary lead is present in varying amount along with the isotope derived from uranium. A hypothesis of elementary evolution is suggested, in which ordinary lead is a product of evolution, the lighter elements condensing in the processes into the heavier elements, and the isotopes formed in radioactive change are products of degradation or decay. The atom being a very highly complex structure, in which the constituents must come together in irregular proportions, the process of evolution from the lighter to the heavier forms is regarded as a slow process in which the final stable configuration is not at once attained, but only after a period of selection of the constituent parts. F. S.

**Mercury Hydrosols produced from Metallic Mercury.** IVAR NORDLUND (*Diss.*, *Upsala*, 1918, 1—125).—The preparation of mercury sols has been studied by a variety of methods, which include (*a*) mechanical dispersion methods, (*b*) thermal dispersion methods, and (*c*) electrical dispersion methods. Under the first group of methods, it is shown that by spirting a fine stream of mercury by means of high pressure into solutions of potassium nitrate and gelatin, definite sols of mercury are produced, although the particles are relatively large. With solutions of ammonia, ammonium chloride, ammonium sulphate, or carbamide, or even pure water, no sol-formation occurred by this method. When mercury is shaken with pure water or with dilute solutions of potassium chloride, sodium chloride, potassium nitrate, potassium sulphate, copper sulphate, mercurous nitrate, or acetic acid, there is no formation of colloidal mercury, but if dilute solutions (ca. $10^{-5}N$) of ammonia, ammonium sulphate, ammonium chloride, calcium citrate, tartaric acid, potassium tartrate, carbamide, or gelatin are used, definite colloidal solutions are produced. Mercury sols are also produced by passing hot mercury vapour directly into water. Mercury sols can be readily prepared by the Bredig method of electrical dispersion, using either direct or alternating current. The law of Stokes is tested for the velocity of fall of a mercury drop through an 11% solution of water in glycerol, and the results show that within the limits of experimental error the law holds for this case. The various sols have been examined in connexion with the distribution of the particles. The sols have varying colours from grey to yellowish-brown and reddish-brown; to characterise the colour of the sols more exactly, the absorption spectrum has been determined over the range $\lambda = 253—263\ \mu\mu$. A number of experiments are described on methods of estimating the purity of the sols produced in different ways, the stability toward various electrolytes, and the stabilising action of electrolytes. From kataphoresis experiments, it is shown that the sols are all positively charged except those prepared in citrate and tartrate solutions, which are negatively charged. J. F. S.

**The Chemistry of Quinquevalent Tungsten.** OSCAR O:SON COLLENBURG (*Zeitsch. anorg. Chem.*, 1918, **102**, 247—276).—By the reduction of tungstic acid or a tungstate in oxalic acid solution with tin, the author has succeeded in preparing soluble, fairly stable complex oxalates containing quinquevalent tungsten. These salts have been isolated in a pure condition, and from them other compounds containing quinquevalent tungsten have been prepared. The reduction with tin proceeds smoothly only in the one stage. It is best to reduce a solution of an alkali tungstate in a concentrated solution of oxalic acid containing slight excess of alkali oxalate. The course of the reduction can be followed by the colour change, through dark blue, green, and yellow to deep red. After removal of tin and excess of oxalic acid, the complex oxalate is precipitated by means of alcohol, and can be purified by dissolving in hot water and salting out, the sodium salt with sodium bromide, the potassium salt with potassium iodide. The compounds must be dried in a current of carbon dioxide, but are fairly stable in air when dry. The sodium salt has the composition $3Na_2O,2W_2O_5,4C_2O_3,12H_2O$, and the potassium salt

$$3K_2O,2W_2O_5,4C_2O_3,9H_2O.$$

They are red, crystalline powders which slowly oxidise in air, and at 100° lose their water, but do not decompose. They are very soluble in water, insoluble in organic solvents. Sodium hydroxide in the cold precipitates from their aqueous solution a brown, amorphous substance containing quinquevalent tungsten, but on boiling, part of this dissolves to form a tungstate, whilst a dark residue remains, probably containing quadrivalent tungsten. The complex oxalates can be regarded as *oxalotungstites*, derived from a hypothetical tungstous acid.

The oxalotungstites dissolve in concentrated hydrochloric acid, forming a deep blue solution, which contains an *oxychloride* of quinquevalent tungsten, probably $WOCl_3$. From this solution, complex chlorides can be isolated containing $WOCl_3$ in combination with chlorides of the alkali metals or ammonium or hydrochlorides of organic bases. The ammonium and potassium salts are precipitated by saturating a hydrochloric acid solution of the corresponding oxalotungstite with hydrogen chloride. The rubidium, cæsium, aniline, tetraethyl- and tetrapropyl-ammonium compounds are precipitated when the corresponding chloride is added to a hydrochloric acid solution of an oxalotungstite, and the pyridine and quinoline compounds are prepared by double decomposition of their hydrochlorides with ammonium chlorotungstite. Four types of complex chlorides have been observed. Type I*a* has the composition $M_2WOCl_5$, in which M may be $NH_4$, Rb, Cs, or $C_6H_5NH_3$; type I*b*, $M_2WOCl_5,xH_2O$, is represented by the potassium compound; type II*a*, $MWOCl_4$, is represented by the pyridine and quinoline compounds, and type II*b*, $MWOCl_4,H_2O$, by tetraethyl- and tetrapropyl-ammonium compounds. The compounds of type I correspond with the so-called molybdenyl chlorides; they form green crystals. Those of type II have no representative among molybdenum compounds; they form shining, brown crystals (II*a*) or bright, greenish-blue crystals (II*b*). The latter hold their water with great tenacity, and may be regarded as hydroxy-compounds, for example, $(C_2H_5)_4N,W(OH)_2Cl_4$. The author prefers to regard the compounds as chloro-derivatives of tungstous acid, rather than as double chlorides or tungstyl chlorides, those of type II being derived from *metatungstous acid*, $WO_2,OH$, and those of type I from the hydroxide, $W(OH)_5$.

The *chlorotungstites* are stable in dry air at the ordinary temperature, but decompose with oxidation to tungstates at 60—70°. They are immediately hydrolysed by water with formation of a brown hydroxide, which has not been analysed. The less soluble cæsium compound is, however, far more stable than the readily soluble ammonium and potassium compounds. They dissolve readily in absolute methyl and ethyl alcohols, with the exception of the rubidium and cæsium compounds, but not in other organic solvents. Concentrated hydrochloric acid and 35% sulphuric acid also dissolve them, but alkalis and ammonia decompose them. Oxidising agents convert them into tungstates, and permanganate and iodine have been employed for quantitative determinations of the quinquevalent tungsten.

The chlorotungstites react vigorously with a concentrated solution of potassium cyanide with evolution of hydrogen cyanide. A reddish-yellow solution is formed containing cyanides of the type $M_4W(CN)_8$, from which a sparingly soluble cadmium compound, $Cd_2W(CN)_8,8H_2O$, has been isolated. A thiocyanic acid compound has also been isolated in the form of a pyridine salt having the composition $(PyH)_2WO(SCN)_5,xH_2O$.

Full details for the preparation of each of the chlorotungstites described are given. E. H. R.

**Behaviour of Solutions of Stannic Fluoride.** N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 906—914).—Stannic fluoride was prepared by the action of anhydrous hydrogen fluoride on stannic chloride according to the method of Ruff and Plato by the use of apparatus involving a minimum amount of platinum. According to observations on the electrical conductivity of its solutions, it hydrolyses much less rapidly than stannic chloride. The conductivity increases rapidly at first, but attains a constant value after some days. The final value corresponds closely with that calculated on the assumption that complete hydrolysis takes place in accordance with the equation $SnF_4 + 4H_2O = Sn(OH)_4 + 4HF$.

Experiments made with a view to ascertain the amount of hydrofluoric acid which is necessary to prevent the precipitation of tin by the action of hydrogen sulphide show that the hydrogen ion concentration must be such that hydrolysis of the stannic fluoride becomes inappreciable. The anomalous behaviour of stannic tin in hydrofluoric acid solution may be explained either by the assumption that stannic fluoride has little tendency to ionise, or by the formation of complex ions of the type $H_nSnF_{4+n}$. Of the two hypotheses, the former seems to be in better agreement with the facts. H. M. D.

**Combinations of Normal Zirconyl Sulphate with some Alkali Sulphates (K,Na,$NH_4$).** ED. CHAUVENET and (MLLE.) H. GUEYLARD (*Compt. rend.*, 1918, **167**, 24—25. Compare this vol., ii, 234).—Normal zirconyl sulphate forms compounds of the types $(ZrO\cdot SO_4)_3,X$ or $(ZrO\cdot SO_4)_3,X_2$, where X may be $ZrO_2$ or an alkali sulphate. The compounds which have been isolated are

$$(ZrO\cdot SO_4)_3,K_2SO_4,8H_2O,$$
$$(ZrO\cdot SO_4)_3,2Na_2SO_4,7H_2O, \text{ and } (ZrO\cdot SO_4)_3,2(NH_4)_2SO_4,7H_2O.$$

W. G.

**Chemistry of Gold at High Temperatures and Pressures.** HAROLD H. MORRIS (*J. Amer. Chem. Soc.*, 1918, **40**, 917—927).—In reference to the explanation of the occurrence of free gold in nature, experiments have been made on the behaviour of gold compounds under the influence of water at high temperatures and pressures. The experiments were made with a specially constructed steel bomb. Gold hydroxide yields metallic gold when treated with water at 322°. In presence of sodium chloride and magnesium chloride, decomposition takes place at a lower temperature; calcium chloride, on the other hand, tends to prevent the decomposition.

Gold chloride may be heated to the critical temperature (370°) before metallic gold appears. In presence of small quantities of sodium, magnesium, or calcium chloride, gold chloride is more stable, and reduction to the metal is not observed until the temperature is raised to 450—460°. The increased stability is attributed to the formation of double chlorides.

Calcite and magnesite become plated with gold when heated with gold chloride solutions up to 310°. Sodium, magnesium, and calcium chlorides prevent this action from taking place until the temperature is raised to about 500°.

Magnesium hydrogen carbonate acts like the normal carbonate, but calcium hydrogen carbonate appears to have no influence on the stability of a gold chloride solution.

It has also been observed that gold dissolves in hot hydrochloric acid containing auric chloride. Aurous chloride is formed.

H. M. D.

## Mineralogical Chemistry.

**The Constitution of Coal.** MARIE C. STOPES and R. V. WHEELER (*Dept. Sci. Ind. Research*, 1918, 1—58).—A monograph in which the subject is dealt with both from the economic and scientific points of view. The points considered are the definition of coal and its general constitution, the principal methods of accumulation of coal-forming vegetable material, the action of solvents on coal, the destructive distillation and distillation at different temperatures, the nature of the liquid distillates, the microscopical evidence on the constitution of coal, the nature of the "ulmic substances," the action of reagents on coal, and the nature of artificial coals. There is a brief discussion of the various theories on the constitution of coal, an appendix on the classification of coals, and a very full bibliography. W. G.

**Augite from Stromboli.** S. Kozu and H. S. Washington (*Amer. J. Sci.*, 1918, [iv], **45**, 463—469).—Dull, black, or brownish-black crystals of augite about 1 cm. long occur loose in some abundance in the volcanic ash around the crater of Stromboli. $D^{19^\circ}$ 3·243. The refractive indices ($\alpha_{Na}=1·693$, $\beta=1·699$, $\gamma=1·719$) are lower than are usual for augite, corresponding with the preponderance of the diopside molecule shown by the following analysis. This analysis (I) corresponds with $Ca(Mg,Fe)Si_2O_6$ 80·12, $(Mg,Fe)SiO_3$ 7·48, $(Mg,Fe)Al_2SiO_6$ 7·03, $NaFeSi_2O_6$ 5·46%. Analysis II is of the basalt scoria in which the crystals occur.

| | $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | NiO. | MgO. |
|---|---|---|---|---|---|---|---|---|
| I. | 50·94 | 0·96 | 3·37 | 2·05 | 7·41 | 0·10 | n.d. | 14·59 |
| II. | 50·83 | 0·81 | 16·66 | 1·52 | 6·64 | 0·12 | n.d. | 6·08 |

| | CaO. | SrO. | $Na_2O$. | $K_2O$. | $P_2O_5$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|
| I. | 20·34 | 0·08 | 0·61 | 0·18 | — | 0·08 | 100·71 |
| II. | 10·99 | — | 2·66 | 2·05 | 1·61 | 0·36 | 100·33 |

L. J. S.

## Analytical Chemistry.

**Universal Gasometer.** Jaroslav Milbauer (*Zeitsch. anal. Chem.*, 1918, **57**, 161—162).—The apparatus described allows the gas contained in it to be delivered at any predetermined rate and constant pressure, the water being admitted through an adjustable constant-level device. W. P. S.

**Mercuric Oxide as a Standard for Volumetric Analysis.** G. Incze (*Zeitsch. anal. Chem.*, 1918, **57**, 176).—A reply to Rosenthaler (this vol., ii, 236). The author's method for using mercuric oxide differs from that described by Rosenthaler and Abelmann. W. P. S.

**Estimation of Halogens, Sulphur, and Nitrogen in the Presence of Mercury.** Maurice François (*Compt. rend.*, 1918, **166**, 1000—1003).—For the estimation of halogens, the mercury is removed by means of zinc turnings by the method previously described (compare this vol., ii, 276), but without using potassium iodide, all the filtrates and decanted liquids being kept and mixed, and in this solution the halogens are estimated by means of silver nitrate in the usual manner.

For the estimation of sulphur, this is first converted into sulphate by oxidation with bromine in hydrobromic acid, and then the mercury and excess of bromine are removed by the addition of zinc turnings, the sulphur being estimated in the filtrate by precipitation as barium sulphate.

Nitrogen in the form of mercuriammonium or mercuriamino-compounds is estimated in the filtrate, after the removal of mercury by the method described (*loc. cit.*), by addition of alkali and distillation of the ammonia or amine into dilute hydrochloric acid and weighing as ammonium chloride or amine hydrochloride.

W. G.

**Volumetric Estimation of Chlorine, Bromine, Cyanogen, and Mercury.** EMIL VOTOČEK (*Chem. Zeit.*, 1918, **42**, 271—272. Compare this vol., ii, 238).—The method described for the titration of chlorides may also be applied to bromides and cyanides, but not to iodides or fluorides; conversely, it may be used for the volumetric estimation of mercury. The insolubility of cupric nitroprusside affords a means of separating this metal from mercury, since mercury nitroprusside is soluble in the presence of an excess of sodium chloride. [See, further, *J. Soc. Chem. Ind.*, 444A.]

W. P. S.

**Estimation of Combined Chlorine in Gastric Juice.** GEORGES and FABRE (*Soc. Pharm. Paris*, 1917; from *Ann. Chim. anal.*, 1918, **23**, 133—134).—Five c.c. of the sample are heated with 10 c.c. of *N*/10-silver nitrate solution, 6 c.c. of saturated potassium permanganate solution, and 10 c.c. of nitric acid; the excess of silver nitrate is then titrated with thiocyanate solution. This gives the total chlorine. Another portion of 5 c.c. of the sample is evaporated in a platinum basin, and the combined chlorine is estimated in the residue as described. The fixed (inorganic chlorine) is estimated in the ash of the sample. Three specimens of gastric juice contained 2·99, 2·84, and 1·09 grams of fixed chlorine per litre, respectively. W. P. S.

**Detection of Iodides in the Presence of Cyanides.** L. J. CURTMAN and C. KAUFMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 914—917).—Comparative experiments made on the detection of iodide in presence of relatively large quantities of cyanide with potassium nitrite, potassium permanganate, hydrogen peroxide, and chlorine as oxidising agents show that the interference of cyanide is least when permanganate is used as the oxidising agent.

If the cyanides are precipitated by the addition of cobalt nitrate and the filtrate examined for iodide by the use of permanganate, sulphuric acid, and chloroform, it is possible to detect 1 part of iodide in presence of 500 parts of cyanide. [See *J. Soc. Chem. Ind.*, 413A.]

H. M. D.

**The Microchemical Method of Estimating Residual Nitrogen.** IVAR BANG (*Biochem. Zeitsch.*, 1918, **87**, 259—263).—The urea can be first extracted from the blood sample on filter paper by treatment with alcohol–ether mixture for five hours, and the remaining nitrogen is then extracted with phosphomolybdic acid solution (0·05% phosphomolybdic acid + 1·5% sulphuric acid) for one hour. The nitrogen in each extract is estimated by the micro-Kjeldahl method. S. B. S.

**Detection of Nitrates in Water.** ESCAÏCH (*J. Pharm. Chim.*, 1918, [vii], **17**, 395).—Fifteen c.c. of the water are mixed with 2 c.c. of 10% antipyrine solution and 4 drops of acid mercuric sulphate solution, and a drop of 5% potassium ferricyanide solution is added. In the presence of 0·1 mg. of nitrite per litre of water, a red coloration is obtained. The reaction is characteristic of nitrites and may be used for the detection of nitrates after these have been reduced by "amalgamated" aluminium. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

**Simplified Working with a Nitrometer.** RUDOLF KAESBOHRER (*Chem. Zeit.*, 1918, **42**, 296).—In the usual gasometric estimation of nitric acid, an approximate correction is made for the pressure due to the acid layer, a depth of 7 mm. of acid being taken as equivalent to 1 mm. of mercury. A more trustworthy procedure is to bring the mercury to the same level in the measuring and levelling tubes, read the volume of the gas, open the tap of the measuring tube, and note the difference in level of the mercury. This difference in mm. is subtracted from the barometric pressure during the experiment. W. P. S.

**Estimation of Nitric Acid in Bismuth Subnitrate.** E. LUCE (*Bull. Soc. chim.*, 1918, [iv], **23**, 264—271; *J. Pharm. Chim.*, 1918, [vii], **17**, 349—359).—At 95° bismuth subnitrate reacts with oxalic acid in the presence of manganese sulphate according to the equation $6(C_2H_2O_4,2H_2O) + 2(BiO{\cdot}NO_3) + H_2SO_4 = 2NO + 3CO + 9CO_2 + 19H_2O + (BiO)_2SO_4$. About 0·5 gram of bismuth subnitrate and 1 gram of manganese sulphate are heated in a flask under a reflux apparatus for one and a-half hours with 50 c.c. of a solution containing 20 grams of crystallised oxalic acid and 60 c.c. of sulphuric acid per 100 c.c.; to prevent secondary reactions, a current of carbon dioxide must be passed through the flask during the reaction. The excess of oxalic acid is then titrated with standardised permanganate solution. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

**Critical Elaboration of Quantitative Precipitation Methods Exemplified by a Method for the Estimation of Phosphoric Acid.** H. HEIDENHAIN (*J. Ind. Eng. Chem.*, 1918, **10**, 426—429).—To determine whether a method is trustworthy, it is necessary to know the solubility of the precipitate and the influence of concentration, temperature, presence of other substances, etc. The purity of the precipitate also requires investigation. In the estimation of phosphoric acid by precipitation with molybdic acid and titration of the precipitate with sodium hydroxide solution, the presence of ammonia interferes with the end-point when phenolphthalein is used as the indicator. It is therefore recommended that the phosphoric acid should be precipitated as potassium phosphomolybdate and the precipitate washed with 10% potassium nitrate solution containing free nitric acid (*N*/100 strength). The small quantity of acid remaining in the filter can be estimated and a correction made. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

**The Wet Method for Estimation of Carbon.** WILHELM STEPP (*Biochem. Zeitsch.*, 1918, **87**, 135—142).—The author discusses the following points in the wet estimation: (*a*) The form of the apparatus. This is figured in the text, and the flask in which decomposition takes place is connected with a condenser to retain the acid. (*b*) The purification of the sulphuric acid. This is accomplished by heating it first with potassium dichromate, and afterwards with permanganate. (*c*) The purity of potassium dichromate used for oxidation of organic salts. It is difficult to obtain this quite free from carbonate. The author substitutes a mixture of chromic acid and sulphuric acid. Finally, when oxidation with the mixture of chromic and sulphuric acids has gone on for four hours, the apparatus is allowed to cool in a current of air free from carbon dioxide, and 10 c.c. of 5°/₀₀ solution of potassium permanganate are added, and the mixture is heated for another hour. S. B. S.

**The Estimation of Carbonates and Hydrogen Carbonates in the Cold; Analysis of a Mixture of these Salts. Exact Details for the Use of Litmus and Phenolphthalein as Indicators.** W. MESTREZAT (*Bull. Soc. chim.*, 1918, [iv], **23**, 250—254).—The author finds that in the titration of carbonates, using phenolphthalein as indicator, a satisfactory and correct end-point is obtained when the whole of the carbonate is just converted by the acid into hydrogen carbonate, if the alkaline liquid is so diluted as not to contain more than 0·07% of sodium carbonate.

Similarly, total alkalinity may be determined by titration in the cold, using litmus as an indicator, if the procedure used is as follows. The standard acid is run in, 1—2 c.c. at a time, until a change in the tint of the indicator is just noticeable. Then between each successive addition of 0·2—0·3 c.c. of acid the liquid is mixed and divided into two parts, one being used as a control and the other receiving the acid. That point at which an addition of acid produces no colour change, as shown by the comparison, is the end-point. W. G.

**Estimation of Sodium and Potassium [in Foodstuffs, etc.].** S. N. RHUE (*J. Ind. Eng. Chem.*, 1918, **10**, 429—431).—The sulphated ash of the substance is dissolved in hydrochloric acid, and after separation of phosphoric acid, iron, calcium, magnesium, etc., the sodium and potassium are weighed together as sulphates. The potassium is estimated in a separated portion of the ash by precipitation as potassium platinichloride after the iron and calcium have been removed. The potassium platinichloride is washed with 80% alcohol, then with 20% ammonium chloride solution saturated with potassium platinichloride (this removes magnesium sulphate and traces of calcium salts), and finally with 80% alcohol. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

**The Lawrence-Smith Method for the Estimation of Alkalis in Silicates.** P. Wenger and Ed. Brange (*Mon. Sci.*, 1918, [v], **8**, I, 97—99).—The Lawrence-Smith reaction for the decomposition of silicates (heating with a mixture of calcium carbonate, 8 parts, and ammonium chloride, 1 part) is complete when the mixture is heated for two hours at 700°. After cooling, the mixture is treated with water, filtered, the calcium is removed from the filtrate, and the alkalis then estimated in the usual way. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

**Detection of Strontium in the Presence of Barium by Calcium Sulphate Solution.** Theodora P. Raikow (*Zeitsch. anal. Chem.*, 1918, **57**, 164—170).—Although strontium sulphate forms slowly when a soluble strontium salt is treated with calcium sulphate solution, the presence of a barium salt, and consequent formation of barium sulphate, greatly increases the rate of precipitation of strontium salt. To detect strontium in the presence of barium, 10 c.c. of the solution to be tested are treated with an excess of calcium sulphate solution, the mixture shaken for fifteen seconds, and then filtered. If the filtrate becomes turbid after a short time, or does so when boiled, strontium is present. In cases where a turbidity is not obtained, the precipitate on the filter should be washed several times with hot water and the filtrate now tested with barium chloride solution; the washing dissolves out any strontium sulphate precipitated with the barium sulphate, and a turbidity is produced on the addition of barium chloride.
W. P. S.

**Precipitation of Magnesium as Oxalate and the Theory of the Formation of Precipitates.** A. Astruc and J. Camo (*J. Pharm. Chim.*, 1918, [vii], **17**, 381—386).—A discussion of the conditions affecting the precipitation of magnesium oxalate. The quantity of this oxalate which is precipitated from magnesium acetate solution by oxalic acid increases with the concentration of the acetate solution. In the separation of large quantities of magnesium salts from calcium salts, the calcium oxalate should be precipitated from a very dilute solution. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

**Hæmatoxylin as a Reagent for Copper Ions and Imperfect Complexes of Copper.** S. Rebello-Alves and A. Benedicenti (*Arch. farm. sper. sci. aff.*, 1917, **24**, 50—57; from *Physiol. Abstr.*, 1918, **3**, 164).—To detect the presence of copper in protein complexes, the solution is treated with a drop of neutral red solution and then with a very dilute solution of sodium carbonate until a clear yellow is obtained, when the solution is sufficiently alkaline for the reaction between hæmatoxylin and copper. S. B. S.

**The Titration of Copper with Potassium Cyanide.** M. P. Applebey and K. W. Lane (*Analyst*, 1918, **43**, 268).—In titrating copper with potassium cyanide, the end-point of the reaction is no longer sharp in the case of solutions containing much less than 1 gram of copper per litre. A method of titrating amounts of about 0·1 gram per litre, however, has been based on the fact that a solution of a double carbonate of copper and an alkali in excess of sodium carbonate solution reacts sharply with cyanide, the end-point of the reaction being shown by the colour changing from blue to an unstable grey, the solution becoming clear and colourless in a few minutes. The double carbonate is prepared by adding the copper solution to a solution of sodium carbonate and sodium hydrogen carbonate, the presence of the latter being necessary to prevent the precipitation of a basic carbonate.

C. A. M.

**Volumetric Estimation of Copper by Potassium Thiocyanate, Potassium Iodide, and Thiosulphate.** G. Bruhns (*Chem. Zeit.*, 1918, **42**, 301—302).—The presence of potassium thiocyanate is of advantage in the iodometric estimation of copper, since it decreases the amount of potassium iodide required. The cupric salt solution is treated with a small quantity of potassium iodide and then titrated with thiosulphate solution containing potassium thiocyanate. The latter reacts with the cuprous iodide first formed and liberates an equivalent amount of potassium iodide, which in turn reacts with a further quantity of the cupric salt. [See, further, *J. Soc. Chem. Ind.*, 446A.] W. P. S.

**A New Method of Estimating Mercury by means of Zinc Filings.** Maurice François (*Compt. rend.*, 1918, **166**, 950—952).—The mercury salt, in a finely divided state, is placed in a conical flask with 1 gram of zinc filings and 10 c.c. of $2N$-sulphuric acid. After half an hour, a second quantity of zinc and acid is added, this being repeated at the end of the first hour. After twenty-four hours, the liquid is decanted through a filter and the residue washed four times by decantation with water. To it is then added, 5 c.c. at a time, 25 c.c. of dilute hydrochloric acid (1:1). After twenty-four hours, this liquid is decanted and 25 c.c. of fuming hydrochloric acid are added. After a further twenty-four hours, the zinc has all dissolved, and the mercury is in the form of one large globule, which is carefully washed by decantation, transferred to a porcelain crucible, and dried first by filter paper and finally over sulphuric acid in the cold, and weighed. The method is accurate and applicable to all mercury salts except the sulphide, which must first be oxidised to the sulphate. It is advisable to add 0·5 gram of potassium iodide to the mercury salt before commencing the estimation. W. G.

**The Use of Hydrofluoric Acid in Analysis.** N. Howell Furman (*J. Amer. Chem. Soc.*, 1918, **40**, 895—906).—A summary is given of the results which have been previously obtained by the use of hydrofluoric acid solutions in the separation of metals by electro-analysis and by precipitation as sulphides. Further results are given which show that copper can be quantitatively separated from vanadium in acid fluoride solution by electro-deposition of the copper. Vanadium thus behaves similarly to tin and tungsten, and preliminary observations indicate that uranium and titanium fall into the same category.

The general chemical behaviour of stannic tin in acid fluoride solutions shows that the stannic ion is not present in appreciable quantity, for such solutions give none of the characteristic reactions of stannic tin. In consequence of this behaviour, hydrofluoric acid may be conveniently used in the analysis of tin–antimony alloys. The procedure recommended is described in detail.

By the addition of boric acid to an acid fluoride solution of stannic tin, the ordinary chemical properties of the stannic ion are developed, and the tin may be quantitatively separated by the action of hydrogen sulphide or by electro-deposition. The boric acid may be replaced by silica with similar results. The action of the boric acid is presumably connected with the formation of borofluoride, and it is shown that acid fluoride solutions to which excess of boric acid has been added have comparatively little action on glass vessels.

The action of boric acid on the behaviour of tin in hydrofluoric acid solution is made the basis of a method for the qualitative analysis of the tin group of metals. [See also *J. Soc. Chem. Ind.*, 445A.] H. M. D.

**Colorimetric Estimation of Lactose in Milk.** August J. P. Pacini and Dorothy Wright Russell (*J. Biol. Chem.*, 1918, **34**, 505—507).—A modification of Lewis and Benedict's colorimetric method for the estimation of dextrose in the blood (A., 1915, ii, 111) is described for the estimation of lactose in milk. [See, further, *J. Soc. Chem. Ind.*, August.] H. W. B.

**Nephelometric Values of Cholesterol and the Higher Fatty Acids.** Frank A. Csonka (*J. Biol. Chem.*, 1918, **34**, 577—582).—The nephelometric value of a substance is defined by the author as the turbidity produced by a given amount of the substance compared in a nephelometer with a given standard within a given length of time. Taking oleic acid as a standard, for example, the nephelometric values of cholesterol, stearic and palmitic acids, are all different, but the nephelometric value of a mixture of any two of them is the sum of the nephelometric values of the constituents. The nephelometric value is influenced by the concentration of acid in the suspension, and the degree of turbidity changes with varying rapidity with the lapse of time. For every substance there is an optimum acid concentration which produces the highest nephelometric value with the least change within a specified interval of time. H. W. B.

**The Colloid Chemistry of Fehling's Sugar Test.** M. H. FISCHER and M. O. HOOKER (*J. Lab. and Clin. Med.*, 1918, **3**, 368—373; from *Physiol. Abstr.*, 1918, **3**, 181).—The varying colours produced by Fehling's solution are ascribed to the different sizes of the reduced copper oxide particles held in suspension. S. B. S.

**Physiology of Blood-sugar. I. Bang's Micro-method of Sugar Estimation.** RICHARD EGE (*Biochem. Zeitsch.*, 1918, **87**, 77—91).—A revision of Bang's method, directing attention more especially to the influence of the time taken in reduction on the results. The following suggestions are made: (1) A longer time than that suggested by Bang ("Methode zur Microbestimmung einiger Blutbestandtheile," 1916). (2) The use of a gas-regulator (figured in text). (3) Strict adherence to standard methods. Attention is also directed to a source of error from the fact that certain substances acting on iodine can be removed from the india-rubber of the apparatus. Methods for avoiding this source of error are indicated. S. B. S.

**The Microchemical Method of Estimation of Blood-sugar.** IVAR BANG (*Biochem. Zeitsch.*, 1918, **87**, 248—258).—The two chief errors in the author's method are due to differences in the intensity of boiling during the reduction, and to the oxidation by air during titration. The first of these can be overcome by passing the gas used for heating through a special form of valve, which is figured in the text, and the second by oxidising the reduced cuprous oxide by excess of potassium iodate and estimating the excess of iodate by titration. The solutions employed are the following: (1) Solution for coagulating the blood (weighed on filter paper by a torsion balance), 1360 c.c. of saturated solution of potassium chloride, 1·5 c.c. of 25% hydrochloric acid, 3 grams of uranyl acetate dissolved in 200 c.c. of water, and the mixture diluted to 2 litres. In this are dissolved 500 mg. of $CuSO_4,5H_2O$. (2) The iodate solution is made by dissolving 0·2230 gram of pure potassium iodate and 50 grams of potassium carbonate in 1 litre of water. (3) *N*/100- or *N*/200-thiosulphate solution. (4) 1% soluble starch, 2% potassium chloride solution. The weighed blood on the filter paper (about 0·1 gram) is extracted by 6·5 c.c. of solution 1. The first extract is poured off, and a second extraction is made with 6·5 c.c. of the solution. Two c.c. of the iodate solution (No. 2) are then added, and the mixture is heated for exactly two minutes. Fifteen seconds before the end of this time, 2 c.c. of 20% (by volume) sulphuric acid are added. After cooling, potassium iodide solution (5%) is added, and titration is carried out by thiosulphate solution (No. 3), using starch (solution 4) as indicator. The difference between the result obtained and the titer of 2 c.c. of the original iodate solution gives the amount of sugar. 0·10 Mg. of dextrose is equivalent to 1·96 c.c. of $N/200$-thiosulphate solution. S. B. S.

**The Microchemical Method of Estimating Dextrose.** IVAR BANG and K. HATLEHOEL (*Biochem. Zeitsch.*, 1918, **87**, 264—272).—The authors find that exact timing of the heating for the reduction process in Bang's method (see preceding abstract) can be avoided by blowing a current of steam through the mixture for four minutes. A slight alteration must be made, however, in the solutions used, especially as regards the amounts of copper sulphate and alkali. The solution for extracting the filter paper containing the blood is as follows: 400 grams of potassium chloride, 3 grams of uranyl acetate, 1·5 c.c. of 25% hydrochloric acid, and 800 mg. of copper sulphate in 2 litres. The iodate solution contains 15 grams of potassium carbonate, 20 grams of potassium ammonium tartrate, and 0·3567 gram of potassium iodate in 1 litre.

S. B. S.

**A Modification of the Selivanov Reaction [for Detection of Ketoses or Sucrose].** F. WEEHUIZEN (*Rec. trav. chim.*, 1918, **37**, 302—303; *Pharm. Weekblad*, 1918, **55**, 831—832. Compare A., 1887, 459).—The reaction may be performed without heating the reacting mixture if a saturated solution of hydrogen chloride in absolute alcohol is used, and to it is added the mixture of sugars, under examination for the presence of a ketose or sucrose, and some resorcinol. A cherry-red coloration appears within three minutes. The method may be applied to the detection of sucrose in milk. [See, further, *J. Soc. Chem. Ind.*, 436A.] W. G.

**Effect of Codeine in Hindering the Precipitation of Morphine by Ammonia from a Solution of its Lime Compound.** H. E. ANNETT and HARDAYAL SINGH (*Analyst*, 1918, **43**, 205—213).—The Pharmacopœia method for the estimation of morphine in opium consists essentially in mixing the sample with calcium hydroxide and water, filtering the mixture, and precipitating the morphine in the filtrate in the presence of ether and alcohol. Codeine also dissolves in the calcium hydroxide solution, and its presence diminishes the quantity of morphine precipitated subsequently by ammonia, the effect increasing with the concentration of the solution and of codeine. The codeine may, however, be removed by extracting the solution with toluene previously to the precipitation of the morphine, and this modification is recommended in the estimation of morphine in opium, particularly in Indian opiums with a high codeine content. Narcotine is quite insoluble in water in the presence of an excess of calcium hydroxide, either alone or mixed with morphine and codeine. W. P. S.

[**Estimation of Histidine in Proteins.**] WALTER E. THRUN and P. F. TROWBRIDGE (*J. Biol. Chem.*, 1918, **34**, 355—356).—See this vol., i, 324.

[**Estimation of Quinine in the Organism.**] HEINZ HARTMANN and LORO ZILA (*Arch. exp. Path. Pharm.*, 1918, **83**, 221—234).—See this vol., i, 328.

**Is the Adamkiewicz Reaction due to Glyoxylic Acid or to Formaldehyde?** E. VOISENET (*Compt. rend.*, 1918, **166**, 789—792).—As opposed to the view of Hopkins and Cole (A., 1901, i, 310), the author considers that the colour reaction is due to the presence of formaldehyde and not of glyoxylic acid. A very dilute solution of formaldehyde readily gives the violet coloration in the presence of a trace of protein. The formaldehyde may be produced in the acetic acid by oxidation. W. G.

**Effect of Time of Digestion on the Hydrolysis of Casein in the Presence of Starch.** J. S. MCHARGUE (*J. Agric. Research*, 1918, **12**, 1—7).—The Van Slyke method for protein analysis, when applied to mixtures of casein and starch, in the proportion of 1:5, which have been hydrolysed from twelve to fifteen hours with 20% hydrochloric acid, gives results for the amino-acid groups that are comparable with those obtained by Van Slyke for casein alone. Prolonging the time of digestion with this strength of acid on such a casein–starch mixture brings about a redistribution of the nitrogen in the histidine and cystine groups. The insoluble residue from the casein–starch hydrolysis contains nitrogen, which is in an inert form and should not be included in the humin determination. W. G.

**Mechanical and Physical Analysis of Soils.** G. RICHTER (*Int. Mitt. Bodenk*, 1916, **6**, 193, 318; from *Bied. Zentr.*, 1918, **47**, 49—52).—A discussion of the various methods for the mechanical and physical examination of soils; Kopecky's trituration method is preferred to that of Atterberg; Breitenbach's method for the estimation of the hygroscopic properties of soils gives higher results than those obtained by Mitscherlich's method. [See, further, *J. Soc. Chem. Ind.*, 384A.] W. P. S.

# General and Physical Chemistry.

**The Scattering of Light in Hydrogen, Oxygen, and Nitrogen.** M. Born (*Ber. Deut. physikal. Ges.*, 1918, **20**, 16—32).—In a previous paper (*ibid.*, 1917, **19**, 243), the author has shown that gases which consist of anisotropic molecules exhibit a scattering effect other than that which has been explained by Rayleigh's theory. The rays which characterise this new type of opalescence are in part non-polarised, and can accordingly be sharply distinguished from the polarised rays which are associated with the more familiar scattering effect. Experiments made by Smoluchowski on hydrogen, oxygen, and nitrogen afforded no evidence of the existence of the effect predicted by the author, and it is supposed that this may be due either to the insufficient anisotropy of the molecules or to the lack of precision in the method of observation.

By reference to the molecular models which have been recently suggested for hydrogen, oxygen, and nitrogen, the author has calculated the magnitude of the effects to be expected, and finds that, although small, it should be possible to observe the scattering effects in question in the case of each of these gases with a suitably designed arrangement of apparatus. H. M. D.

**Refractivities of Saturated and Unsaturated Compounds.** Gervaise Le Bas (*Trans. Faraday Soc.*, 1918, **13**, 414—419. Compare this vol., ii, 49).—From a comparison of the molecular refractivities of corresponding derivatives of benzene and of the saturated cyclic hydrocarbons, it is found that the augmentations due to substitution in the benzene ring are considerably greater than those which accompany substitution in rings of the polymethylene series. In this connexion, it may be noted that the unsubstituted saturated cyclic hydrocarbons show no anomaly in refractive power, whether the ring system is simple or complex.
H. M. D.

**Ketonic and Enolic Modifications of Compounds.** Gervaise Le Bas (*Trans. Faraday Soc.*, 1918, **13**, 420—423).—The constitution of various keto-enol tautomerides is considered in relation to their refractivities. The molecular refractivities of acetylacetone, methylacetylacetone, ethyl oxaloacetate, ethyl mesityloxido-oxalate, methyl cyanoacetoacetate, ethyl acetylmalonate, ethyl acetonedicarboxylate, and ethyl β-hydroxy-α-phenylacrylate and its acetate lead to the conclusion that these substances exist in one form only, and that the different isomerides appear to be mutually exclusive. H. M. D.

**Presence in the Solar Spectrum of the Water Vapour Band λ 3064.** A. Fowler (*Proc. Roy. Soc.*, 1918, [*A*], **94**, 472—475).—A comparison is made of the lines composing the band λ 3064, which is always obtained in the spectra of gases containing both hydrogen and oxygen, with the lines of the solar spectrum in this region as plotted and measured by Rowland. It is shown that, despite the interference of certain metallic lines, this band is also present in the solar spectrum. J. F. S.

**The Ultra-violet Band of Ammonia and its Occurrence in the Solar Spectrum.** A. Fowler and C. C. L. Gregory (*Proc. Roy. Soc.*, 1918, [*A*], **94**, 470—471).—Photographs of the ammonia spectrum have been made by burning a copper arc in an atmosphere of ammonia. From these, it is shown that the ammonia spectrum consists of a main band, which is made up of a bright central maximum at λ 3360, a secondary maximum at λ 3371, and a number of lines, arranged in groups of three, which extend to a considerable distance in both directions. The lines composing the maxima are very closely crowded, and are found to be arranged in series of ordinary type. The components of the groups of three are widely separated near the central maximum, but the intervals rapidly diminish, and there is finally coalescence at λ 3450 towards the red and at λ 3287 towards the violet, where the lines fade out. This spectrum has been compared with the *P*-group of the solar spectrum, and shown to be practically identical; hence the presence of ammonia in the absorbing atmosphere of the sun is definitely established. J. F. S.

**The Ultra-red Absorption Spectrum of Water Vapour.** Gerhard Hettner (*Ann. Physik*, 1918, [iv], **55**, 476—496).—Measurements of the absorption of ultra-red rays by water vapour have been made for the region extending from the visible spectrum to a wave-length of 34 μ. An improved arrangement of apparatus for the investigation of absorption in the long-waved region is described. The results recorded show the existence of 78 maxima, of which only 20 have been recorded by previous observers. The wave-lengths of the maxima are tabulated, and a curve is given which shows the absorption relations in detail. H. M. D.

**Characteristic Ultra-red Vibrations of Nitrates.** Clemens Schaefer and Martha Schubert (*Ann. Physik*, 1918, [iv], **55**, 577—588).—The reflection spectra of sodium nitrate, potassium nitrate, rubidium nitrate, lead nitrate, barium nitrate, and mercurous nitrate have been determined with polarised light and ordinary light. All six substances show three maxima, at approximately 7·5 μ, 12·5 μ, and 15·0 μ; in addition, mercurous nitrate shows a fourth maximum at 10·08 μ with ordinary light. From the examination with polarised light, it is shown for the biaxial nitrates that the three maxima observed with ordinary light are made up of three components corresponding respectively with the vibrations parallel to the axes of the three indices of refraction. The characteristic vibrations, as in the case of the carbonates and sulphates (A., 1916, ii, 506), depend very slightly on the metal and are due to internal vibrations of the $NO_3$ group, which are practically the same in all the nitrates examined. The similarity between the space gratings of sodium nitrate and calcium carbonate, as put forward by Bragg, is discussed in the light of abnormalities found in the present work. J. F. S.

**The Distribution of Intensity in Series Spectra Excited by Cathode Rays.** J. Holtsmark (*Ann. Physik*, 1918, [iv], **55**, 245—298).—The fact that previous attempts to measure the changes in the distribution of the intensity in series lines under the influence of varying conditions have not led to consistent results is attributed to errors introduced by the method of excitation. New experiments have been made on the Balmer series with cathode rays as the exciting agent, and the results indicate that the relative intensities of the series lines are, in these circumstances, independent of the current strength and also of the fall of potential. On the other hand, it is found that the lines of longer wave-length become relatively more intense as the pressure of the hydrogen increases. The connexion between the pressure $p$ and the ratio $K$ of the intensities of the lines $H_\beta$ and $H_\gamma$ is expressed by the equation $Kp^{-0\cdot125}=\text{constant}$. The pressure effect is not obtained when the increase of pressure is brought about by the addition of another gas to the hydrogen. Experiments in which the hydrogen was mixed with iodine, oxygen, argon, and helium respectively, all gave negative results in that these gases produced no change in the relative intensities of $H_\beta$ and $H_\gamma$. On the other hand, observations made on the series lines of helium at different pressures showed a pressure effect similar to that found in the case of hydrogen.

The theoretical interpretation of the pressure effect is discussed, and the author concludes that Bohr's hypothesis relative to the origin of the effect is not in agreement with the observations.

H. M. D.

**Electron Theory of the Natural Optical Rotatory Power of Isotropic and Anisotropic Liquids.** M. Born (*Ann. Physik*, 1918, [iv], **55**, 177—240).—A theoretical paper in which the author's previous attempts (compare A., 1915, ii, 659) to explain the natural rotatory power of optically active substances on a molecular basis in terms of electrons are more completely developed. The general formulæ derived are discussed in reference to the nature of the molecular forces and the symmetry relations, and are applied to the consideration of isotropic liquids with natural rotatory power, of liquids rendered anisotropic by means of an electric field, and of liquids which are normally anisotropic (liquid crystals).

H. M. D.

**Colour Determination of Faint Luminescence.** Harry B. Weiser (*J. Physical Chem.*, 1918, **22**, 439—449).—A method of determining the colour of faint luminescence is described which consists in photographing the luminescence on a panchromatic plate and interposing a series of colour screens between the source of light and the plate. The method may be used in all cases when the glow is uniform and sufficiently strong to affect a highly sensitive photographic plate.

The results obtained in the investigation of the chemiluminescence emitted in the oxidation of alkaline pyrogallol by hydrogen peroxide, of phosphorus in acetic acid solution by hydrogen peroxide, and of amarine in alkaline alcoholic solution by chlorine and bromine, are described in detail. The crystalloluminescence emitted when a saturated aqueous solution of sodium chloride is mixed with alcohol or hydrochloric acid was also examined, with the result that the colour of the light is shown to be bluish-violet. H. M. D.

**Photolysis and Electrolysis.** EMIL BAUR (*Helvetica Chim. Acta*, 1918, 1, 186—201).—A theoretical paper in which the author evolves an electrolytic theory to explain the mechanism of photolysis. A substance which has been subjected to light has set up a molecular potential difference, and as such is capable of effecting a chemical reaction. Photolysis is therefore to be regarded as molecular electrolysis. Thus the decomposition of Eders's solution by eosin in light is to be regarded as a cathodic reduction of mercuric chloride to calomel and an anodic oxidation of oxalic acid to carbon dioxide, which may be expressed:

$$\text{Eosin}\begin{cases} \oplus + \tfrac{1}{2}C_2O_4'' = CO_2 \\ \ominus + HgCl_2 = HgCl + Cl' \end{cases}$$

The author then proceeds to calculate the value of the *E.M.F.* operative on the basis of the quantum theory and the assumption that only one energy quantum may be absorbed. The following values are obtained for the lines mentioned: Sodium line, $\lambda = 589\ \mu\mu$, $E = 2{\cdot}4$ volts; mercury line, $\lambda = 435\ \mu\mu$, $E = 3{\cdot}2$ volts; Hg (fluorescent line), $\lambda = 253{\cdot}6\ \mu\mu$, $E = 5{\cdot}5$ volts; and $\gamma$-rays, $\lambda = 0{\cdot}012\ \mu\mu$, $E =$ about 100,000 volts. A large number of cases are considered in the light of this hypothesis. J. F. S.

**Absorption of *X*-Rays.** E. A. OWEN (*Proc. Roy. Soc.*, 1918, [A], **94**, 510—524).—According to Bragg and Pierce (A., 1914, ii, 792), the atomic absorption coefficient $A$ is connected with the atomic number $N$ of the absorber, and the wave-length $\lambda$ of the radiation by the equation $A = CN^4\lambda^{5/2}$, in which $C$ is constant over considerable ranges of wave-length, but changes abruptly in the region of selective absorption. From the investigation of the absorption of a large number of aqueous solutions, Aurén (A., 1917, ii, 350) has recently deduced values for the atomic absorption coefficients of the elements which lead to the conclusion that with respect to the magnitude of the absorption coefficient, the elements may be divided into groups, for each of which the atomic absorption coefficient is directly proportional to the atomic number. An attempt is made to account for these discordant results.

The ordinary absorption coefficient is a composite quantity which represents the sum of the fluorescent absorption coefficient and the scattering coefficient. Assuming that the latter has a constant value equal to 0·2, in agreement with the results obtained by Barkla for the light elements and radiation of widely varying wave-length, the author calculates from his observations the values of the atomic fluorescent absorption coefficient, and finds that this is nearly proportional to the fourth power of the atomic number of the absorber. Since it is known that the fluorescent absorption coefficient varies as the cube of the wave-length of the absorbed radiation, the connexion between the atomic fluorescent absorption coefficient $A_f$, the atomic number $N$, and the wave-length $\lambda$ may be expressed in the form $A_f = CN^4\lambda^3$, where $C$ remains constant over certain ranges of wave-length, but changes abruptly at critical points. This equation differs from that put forward by Bragg and Pierce in that the coefficient $A_f$ is independent of the scattering of the radiation and refers only to the loss of energy of $X$-radiation resulting from the production of corpuscular radiations and the fluorescent $X$-radiations which accompany them.

The author's measurements were made on zinc, copper, nickel, iron, aluminium, magnesium, water, and filter-paper with radiation of wave-length $\lambda = 0·586 \times 10^{-8}$ cm. ($\alpha$-line of palladium), and the values obtained for the total absorption coefficients agree fairly closely with those recorded by Bragg and Pierce (*loc. cit.*).

It is further shown that, if the scattering coefficient is assumed to have a constant value of 0·2 for all elements from hydrogen to bromine, the equation $A_f = CN^4\lambda^3$ leads to values for the total absorption which are in close agreement with those obtained in the experiments of Aurén. H. M. D.

**The Positive Ion as Carrier in the Canal Ray Fluorescence of Inorganic Salts.** SVEN EM. OHLON (*Ber. Deut. physikal. Ges.*, 1918, **20**, 9—15).—When inorganic salts are subjected to the action of cathode rays of sufficiently high velocity, the salts fluoresce with the emission of the line spectrum of the metal present in the salt. For different salts of the same metal, the cathode ray energy required for this emissive effect increases with the heat of formation of the salt. The cathode ray energy at which emission begins is found to diminish as the discharge potential increases.

A similar series line emission occurs when inorganic salts are bombarded by canal rays, but the energy of the canal rays required to produce this effect varies to only a small extent when different salts of the same metal are employed, and the variation with magnitude of the discharge potential is also much smaller than in the case of cathode ray bombardment.

The observed differences suggest that the cause of the emission may not be the same in the two cases, and experiments have been devised with the object of elucidating further the changes which occur under the influence of canal rays. In these, the canal rays were allowed to fall on the powdered salt contained in a small aluminium dish supported in the discharge tube in the path of the canal rays. The dish was connected through a galvanometer to earth, and a small direct-vision spectroscope was focussed on the bombarded salt. The discharge potential was varied, and by taking readings of the galvanometer, it has been found that the emission of the series lines is accompanied by a diminution in the positive current which flows through the galvanometer. This sudden change in the current, which characterises the transition from the non-fluorescent to the fluorescent condition, has been found to occur with salts of sodium, lithium, magnesium, calcium, strontium, barium, cadmium, and copper. The observations afford support for the view that the canal ray fluorescence is due to the metal ions which result from the dissociation of the salt under the influence of the canal rays. The carriers would thus appear to be the same for both cathode ray and canal ray fluorescence.

H. M. D.

**Periods, Atomic Masses, and Electric Charges of the Radioelements.** EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1918, **92**, 685—716).—A theoretical paper in which a number of regularities between the valency, average life, and ray emission of the radioactive elements are put forward. In each disintegration series, those elements which emit α-rays and have even valencies have longer average lives the greater the atomic mass. Of those pairs of elements which emit α-rays and have contiguous valencies (that is, IV, V), that with the smaller valency has the greater average life, whether the atomic mass of the pair is the same or not. Of two directly following β-ray changes, the first proceeds more slowly than the second, that is, the element with the smaller valency has the longer life. In the same disintegration series, elements which emit β-rays have longer lives the greater the atomic mass, whether the valency is odd or even, the odd and even valencies being considered separately. A similar rule holds for elements in the same group of the periodic system, but not in the same pleiad, with certain exceptions. There are very few exceptions to the above statements, and these occur generally in the least well investigated elements. The origin and atomic mass of actinium are discussed, and reasons are advanced for the value 226. The author also discusses the identity of isotopes and analogous radioactive elements, and finally the relationship of the radioactive elements to the periodic classification. J. F. S.

**Ionisation of Gas during a Chemical Reaction.** ALEXANDRE PINKUS (*Helvetica Chim. Acta*, 1918, **1**, 141—145; *J. Chim. Phys.*, 1918, **16**, 201—227).—With the object of ascertaining whether ionisation occurs during the interaction of two gases, the author has brought the following pairs of gases, (1) nitric oxide and oxygen, and (2) nitric oxide and chlorine, together in a large glass globe under a pressure of 0·25—0·5 atm. The walls of the vessel were connected by iridioplatinum electrodes with a sensitive electrometer, and the rate of discharge was plotted. In the case of nitric oxide and oxygen, no formation of ions takes place, nor is there any evidence that ionisation occurs during the reaction between chlorine and nitric oxide if the chlorine is not in excess. Should the chlorine be in excess, there is a marked ionisation. The author attributes the ionisation to the intermediate formation of $NOCl_2$. J. F. S.

**Resonance and Ionisation Potentials for Electrons in Sodium Vapour.** JOHN T. TATE and PAUL D. FOOTE (*J. Washington Acad. Sci.*, 1918, **7**, 517—525).—In the further investigation of the potentials at which electrons give rise to the emission of rays, experiments have been made on sodium vapour. The resonance potential at which rays corresponding with the *D*-lines are emitted is found to be 2·12 ± 0·06 volts, the value calculated on the basis of Bohr's theory being 2·10 volts. When the potential reaches 5·13 ± 0·1 volts, ionisation of the sodium vapour occurs. This is identical with the value calculated on the basis of Bohr's theory by using the limiting wave-length of the principal series of lines in the sodium spectrum.

The lower potentials found by Wood and Okano (*Phil. Mag.*, 1917, [vi], **34**, 177) in their observations on the emission of the *D*-lines by sodium vapour suggest that ionisation of the vapour occurs under the influence of more slowly moving electrons. A full account of this and the previous paper (A., 1918, ii, 94) is to be found in *Phil. Mag.*, 1918, [vi], **36**, 64—75. H. M. D.

**Relation of the Electrical Conductivity to the Periodic System of the Elements.** E. GRÜNEISEN (*Ber. Deut. physikal. Ges.*, 1918, **20**, 53—62).—According to Benedicks (*Jahrb. Radioaktiv. Elektronik.*, 1916, **13**, 351), the atomic conductance, measured by the product of the specific conductance and the atomic volume, is a periodic function of the atomic weight. The conductance data used by Benedicks are not strictly comparable, however, for the influence of temperature is by no means the same for the different elements. It is suggested that conductance data for corresponding temperatures should be used in the comparison of the atomic conductances, and in accordance with the empirical formula referred to in the following abstract, such temperatures are those which bear the same ratio to the characteristic temperatures.

By reference to the data which are available for this comparison, it is shown that the atomic conductance is a periodic function of the atomic weight, and that the value decreases from the first to the eighth group in the periodic table. H. M. D.

**Electrical Conduction of Metals at Low Temperature.** E. GRÜNEISEN (*Ber. Deut. physikal. Ges.*, 1918, **20**, 36—52. Compare A., 1913, ii, 377).—By reference to the data for lead, cadmium, zinc, mercury, gold, platinum, silver, and copper, the author has tested the empirical formula $w \sim T \,.\, F(T/\Theta) \,.\, C_p/C_v$ for the influence of temperature on the electrical resistance of metals. In this formula, $w$ represents the resistance, $T$ the absolute temperature, $F(T/\Theta)$ a universal function of $T/\Theta$, where $\Theta$ is the characteristic temperature of the metal according to Debye's theory. It is shown that the formula affords a satisfactory account of the observed variations in the conductivity of metals over a wide range of temperature, and the author infers that the empirical expression affords a close approximation to the statement of the actual law which connects conductivity and temperature. H. M. D.

**Electronic Theory of the Metals.** TH. WEREIDE (*Ann. Physik*, 1918, [iv], **55**, 589—607).—A theoretical paper in which the electronic theory of metals is discussed. It is shown that, apart from a numerical correction, Drude's formula for electric conductivity is unassailable. The formula $x = \frac{1}{2} \,.\, e^2/m \,.\, nl/v$ has been modified by eliminating the three unknown, $n$, $l$, and $v$, and in their place introducing the three atomic constants $\nu$ = vibration number of an atom, $\epsilon$ = emission number of an atom, and $a$ = absorption coefficient of an atom. The constant $a$ bears the relationship $a = c\alpha$ to Lenard's coefficient $\alpha$, where $c$ is the number of atoms per c.c. The Lenard theory gives then the formula $x = e^2\epsilon/6ca^2 \,.\, (e^{h\nu/kT} - 1)h\nu$ for the electric conductivity and a similar formula for thermal conductivity. On the basis of this formula, the reasons for the following points are explained. (1) At high temperatures, the electric resistance is approximately proportional to the absolute temperature. (2) The change in resistance depends on the energy change of the substance. (3) The resistance approaches zero at the absolute zero. (4) The conductivity curve and the atomic volume curves have a similar form. (5) Under similar conditions, the conductivity is greater the greater the electro-affinity of the atoms. J. F. S.

**Calculation of the Position of the Conductivity Minimum in Neutralisation.** W. D. TREADWELL (*Helvetica Chim. Acta*, 1918, **1**, 97—110).—The author has calculated the position of the conductivity minimum in the neutralisation of (1) a diluted strong acid by a diluted strong base, (2) a weak monobasic acid by a diluted mono-acidic strong base, (3) a mixture of two weak monobasic acids of different strengths by a strong mono-acidic base, and (4) a mixture of a monobasic weak acid and a monobasic strong acid by a strong mono-acidic base. In the first case, the minimum of conductivity lies exactly at the point of neutralisation; in the second case, using equal concentrations of acetic acid and alkali, the minimum occurs when there is an excess of 0·4% of acid present, or generally if $x$ represents the number of c.c. of alkali of concentration $c_2$ which is present to 1 c.c. of acid of concentration $c_1$, then $x = c_1/c_2 \times k_1/k_1 + \sqrt{k} \,.\, l_{OH}/l_H$. The influence of decreasing strength and concentration of the acid on the position of the minimum is also calculated. The conductivity minimum is calculated in the case of a number of acids, and these values are compared with the experimental values of Thiel and Roemer. Good agreement is found between the two sets of values. J. F. S.

**Calculation of the Electrochemical Normal Potential.** KARL F. HERZFELD (*Ann. Physik,* 1918, [iv], **56**, 133—160).—A mathematical paper in which the normal potential of the ions is calculated on the assumption that the entropy constant of the dissolved ions is the same as that of the corresponding atoms. The numerical results of this calculation differ from the experimental values, but the amount of divergence is the same for ions of equal mobility. The divergences are therefore attributed to complex formation of the ions with water. From these calculations, formulæ for the solubility of salts are deduced. In open cells, only the positive ions are in equilibrium, for the electrons only slowly reach equilibrium; hence the cell at first only approximates to a reversible element. In this connexion, the mechanism of the semi-permeable membrane is discussed. Calculations are made for metals of the single potential, the contact potential, and the electron number. The Helmholtz equation is not strictly applicable to single electrodes. J. F. S.

**[Potentials due to the Flow of Electrolytes through Capillary Tubes and the Stability of Colloids.]** H. R. KRUYT (*Kolloid Zeitsch.*, 1918, **22**, 81—98).—The potential differences produced by the flow of solutions of electrolytes through a capillary tube have been measured in experiments with solutions of different chlorides. In the apparatus used, the capillary tube formed part of the connexion between two glass vessels fitted with silver electrodes coated with silver chloride, and the chloride solution was made to pass through the glass capillary from one vessel to the other under the influence of a constant pressure difference.

The results obtained with solutions of potassium, barium, and aluminium chloride show that the influence of the cation on the potential difference between the electrodes depends very largely on the valency of the cation. The relations are in general very similar to those which were found by Powis (A., 1915, ii, 137) in the investigation of the influence of the three chlorides on the cataphoresis of hydrocarbon oil emulsions. In both series of observations, the effects are attributable to the adsorption of electrolytes. The author's experiments seem to show, however, that in very dilute solutions the contact potential is increased by the presence of the electrolyte. It is probable that this fact explains the well-known peptonising action of electrolytes in very dilute solution and the essential importance of small quantities of electrolytes in connexion with the stability of colloidal systems. H. M. D.

**Passivity of Chromium. II.** A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1119—1134. Compare this vol., ii, 183).—In the further investigation of the electrochemical behaviour of chromium, measurements have been made of the potential of chromium when subjected to anodic and cathodic polarisation.

The phenomena associated with the anodic polarisation of electrolytic chromium depend to some extent on the nature of the metal on which the chromium has been deposited. If the metal immersed in a solution of chromous sulphate is anodically polarised with a sufficiently strong current, the chromium becomes passive, but when the current is interrupted, the potential of the metal is found to be more negative than before polarisation. The passivation during anodic polarisation and activation after this treatment are shown by chromium which has been deposited on copper, silver, or gold. The degree of activation after anodic polarisation increases with the strength of the polarising current.

Chromium, prepared by Goldschmidt's process, which has been activated by treatment with molten zinc chloride, or a mixture of sodium and potassium chlorides, may be anodically polarised in a solution of potassium chloride without becoming passive. The resistance offered by the metal to the action of the polarising current is greater when the strength of the current is gradually increased than when the current strength is increased rapidly. The resisting power of the metal is smaller when the chromium has been previously subjected to cathodic polarisation. If the chromium has been rendered passive by anodic polarisation in a solution of potassium chloride, the active condition may be restored by heating the solution. This change occurs even when the polarising current is continued during the heating of the solution, and, on cooling, the chromium remains in the active condition provided that the current is not too strong. H. M. D.

**Allotropy of Cadmium. VI.** ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1177—1185).—A criticism of the conclusions drawn by Getman from his observations (compare A., 1917, ii, 533) on the *E.M.F.* of $Cd|CdSO_4|Cd$ amalgam cells. According to Getman, the influence of temperature on the *E.M.F.* of cells containing 8% cadmium amalgam points to the existence of two allotropic forms of cadmium with a transition point at 37·5°. The discontinuity in the temperature coefficient of the *E.M.F.* at this temperature is, however, to be attributed to a change in the amalgam at this temperature. According to Bijl's investigations (A., 1903, ii, 6), the 8% amalgam used by Getman undergoes transformation at about 40°, and the resulting change in the electromotive behaviour of the amalgam has been erroneously attributed by Getman to the transformation Cd-α into Cd-β. The actual results obtained by Getman are considered to afford confirmation of the views which have been previously put forward by the author as a result of his investigation of the allotropy of cadmium (A., 1914, ii, 52, 652; 1915, ii, 40, 144). H. M. D.

**Magnetic Susceptibility and Electric Resistivity.** F. H. Loring (*Chem. News*, 1918, **117**, 229—231).—A theoretical discussion of magnetic susceptibility in which the author assumes that ferro-, para-, and dia-magnetic qualities are to be explained in terms of atomic and molecular currents which are dependent on the specific resistances of the elements concerned. H. M. D.

**The Influence of the Finite Volume of Molecules on the Equation of State.** Megh Nad Shaha and Satyendra Nath Basu (*Phil. Mag.*, 1918, [vi], **36**, 199—202).—Starting from Boltzmann's entropy principle, the authors have obtained a new equation of state which may be written in the form $pV = NK\theta x/1 - e^{-x}$, where $x = \beta p/K\theta$. In these equations, $K$ represents Boltzmann's gas constant, $N$ the number of molecules contained in volume $V$, $\theta$ the temperature, and $\beta = 8 \times$ volume of a single molecule. From this equation of state, the critical volume $V_c = 3{\cdot}166b$ and $K = 3{\cdot}513$. The values of $V_c$ derived from the van der Waals and Dieterici equations are $3b$ and $2b$ respectively, and the values of $K$ 2·66 and 3·695 respectively. H. M. D.

**The Course of the Values of *a* and *b* for Hydrogen at different Temperatures and Volumes. II.** J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1195—1212. Compare this vol., ii, 185).—A theoretical paper in which the pressure–volume relations are further discussed in reference to the variability of $a$ and $b$. H. M. D.

**Isothermals of Monatomic Substances and their Binary Mixtures. XIX. Vapour Pressures of Neon between the Boiling Point and the Critical Point.** P. G. Cath and H. Kamerlingh Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1160—1162).—The vapour pressures of liquid neon have been measured at temperatures ranging from 24·42° to 44·43° (abs.). The results are satisfactorily reproduced by the formula $T \log p = -65{\cdot}061 + 2{\cdot}8191T + 0{\cdot}01118T^2$, where $p$ denotes the vapour pressure in atmospheres.

A comparison of the reduced vapour pressure curves for oxygen, nitrogen, argon, neon, and hydrogen has been made, and from this it appears that the divergence between hydrogen and neon is much greater than that between neon and argon, in spite of the fact that the critical temperature of neon is relatively low.

H. M. D.

**The Characteristic Equation of Fluids.** Pierre Weiss (*Compt. rend.*, 1918, **167**, 232—235. Compare *ibid.*, 1918, **167**, 78).—The isochores for air, ethylene, ether, and *iso*pentane are given, and in each case they consist of rays of straight lines each showing one point of inflection. They resemble the magnetic isotherms (*loc. cit.*). W. G.

**The Entropy of a Metal.** H. Stanley Allen (*Proc. Physical Soc. London*, 1918, **30**, 215—220).—The formula derived by Ratnowsky (*Ber. Deut. physikal. Ges.*, 1914, **16**, 1033) for the entropy of a substance in the solid state is found to give values for a number of metals in very close agreement with those recorded by Lewis and Gibson (this vol., ii, 29). The assumptions made by Ratnowsky in deducing his entropy formula are examined, and the conclusion is drawn that these are justified as being at least approximately true. H. M. D.

**Boundaries of Existence of the Liquid State.** Julius Meyer (*Zeitsch. Elektrochem.*, 1918, **24**, 138—139. Compare Herz, this vol., ii, 150).—A criticism of Herz's definition of the boundaries of the liquid state. Herz makes the melting point and the critical point the limits of existence of a liquid, whereas Meyer is of opinion that no such points can be specified. J. F. S.

**Boundaries of Existence of the Liquid State.** W. Herz (*Zeitsch. Elektrochem.*, 1918, **24**, 139. Compare preceding abstract).—Polemical; an answer to Meyer (*loc. cit.*). J. F. S.

**Boiling Points of the Paraffins.** Gervaise Le Bas (*Chem. News*, 1918, **117**, 241—242).—A theoretical paper in which it is shown that the rule of Hinrichs and Naumann, which states that the more the chain of a molecule is branched the lower will be the boiling point, is not generally to be followed. It is shown that the boiling point depends on whether the hydrogen attached to the β-, γ-, δ-, etc., carbon atoms has been displaced by methyl groups. In dealing with this question, it is necessary to consider the formulæ of *iso*-compounds. It is the practice of writing the formula of an *iso*-compound thus, $\genfrac{}{}{0pt}{}{\mathrm{Me}}{\mathrm{Me}}\!>\!\mathrm{CHR}$, which tacitly assumes that it consists of two similar methyl groups attached to one carbon atom. From the point of view of the boiling points, this is not true. This class of structure involves the displacement of an hydrogen atom attached to the α-, β-, γ-, δ-, etc., carbon atom of the hydrocarbon by a single methyl group. The difference in boiling point due to this structure is 6° or 7° when substitution of a β-methylene group has been effected, and slightly more, 9°, when the γ-methylene group has been substituted. J. F. S.

**Method for the Determination of the Relation between Vapour Pressures and their Corresponding Temperatures at Pressures of less than Five Millimetres.** W. R. Ham, J. C. Churchill, and H. M. Ryder (*J. Franklin Inst.*, 1918, **186**, 15—28).—The substance under investigation is subjected to slow distillation and condensation in a closed system of considerable capacity, the pressure in which is reduced to a low value determined with the aid of a McLeod gauge which is attached to the closed system. The system is also connected with a reservoir of pure dry hydrogen, the object of this arrangement being to ensure accuracy in the readings of the McLeod gauge. The pressure in the apparatus is varied by running the pump at different speeds, the driving motor being suitably controlled. The liquid in the distilling flask is electrically heated by passing a current through a platinum wire immersed in the liquid, and the vapour evolved passes through a side-tube, in which a thermometer is supported, to a condenser, from which the condensate drops into a receiver. For a given rate of working of the pump, a series of observations is made in which the liquid is distilled at different rates determined by the number of drops of liquid which fall from the end of the condenser tap into the receiver in a fixed interval of time. In each of these experiments, the temperature of the vapour registered by the thermometer is recorded. By plotting the temperature against the rate of distillation, a smooth curve is obtained, and by extrapolation to zero rate of distillation, a temperature is obtained which corresponds with the pressure in the closed system as measured by the McLeod gauge.

Results obtained for acetophenone by this method show close agreement with the values obtained for this substance by Kahlbaum, who measured the depression of a barometric column. The results may be expressed by the equation $\log P = 19 \cdot 696 - 72 \cdot 540 \times 0 \cdot 993944^T$, or by the equation $\log P = 16 \cdot 152 - 3390 \cdot 96/T - 534192 \cdot 38/T^2$. H. M. D.

**The Solutions of Gases in Liquids.** FÉLIX MICHAUD (*Ann. Physique*, 1918, [ix], **9**, 203—232, 233—258. Compare A., 1917, ii, 122).—A theoretical discussion of the subject. Contrary to Duhem's conclusions, the presence of a gas in solution at constant temperature does not always lower the vapour pressure of the solvent. That only occurs if the pressure of the solution is maintained constant by means of an auxiliary, insoluble gas. It is possible to obtain a simple formula from which the vapour pressure of the solvent can be calculated in terms of the pressure of the gas, the formula being really an expression of Raoult's law for a very soluble, normal gas which obeys Henry's law. A cryometric study of solutions of gases leads to similar results.

From a study of the calorific phenomena which accompany the solution of a gas, a simple expression for the entropy of reversible solution can be obtained. A formula is also established connecting the specific heat of a solution of a gas in a liquid with the coefficient of solubility of the gas. W. G.

**Iso-piestic Solutions.** W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1918, **13**, 401—410).—Solutions of various salts were placed in an exhausted desiccator and allowed to remain at constant temperature until the several solutions were in equilibrium with one another. The resulting solutions have the same vapour pressure at the temperature of the experiments, and are termed iso-piestic.

Results obtained at 18° show that iso-piestic solutions of potassium chloride, sodium chloride, and lithium chloride contain different numbers of molecules of water per molecule of salt. The value of this molecular ratio ($h$) for a saturated solution of potassium chloride is 12·41, whilst for the iso-piestic solutions of sodium chloride and lithium chloride $h = 14{\cdot}16$ and 17·07 respectively. Although the total quantities of water thus differ appreciably for the three salts, it is calculated that the quantities of uncombined water are very nearly the same. The differences in $h$ are due to differences in the quantities of combined water, for which the respective molecular ratios are approximately 1, 3, and 6.

Observations in which the dry salts were exposed to the action of water vapour at different pressures lead the author to the conclusion that for substances which do not form crystalline hydrates there is, at a given temperature, a certain pressure of aqueous vapour below which the dry substance will not take up water vapour, and if the substance is not dry originally, it will become so provided the pressure of aqueous vapour is lower than this critical value, which is called the critical hydration pressure of the substance. H. M. D.

**Measurement of Very Low Temperatures. XXVII. Vapour Pressures of Hydrogen in the Neighbourhood of the Boiling Point and between the Boiling Point and the Critical Temperature.** P. G. CATH and H. KAMERLINGH OMNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1155—1159).—The vapour pressures of liquid hydrogen have been determined at temperatures between 24·59° and 32·93° (abs.). The results obtained are satisfactorily represented by the formula $T \log p = -56{\cdot}605 + 3{\cdot}80157T - 0{\cdot}10458T^2 + 0{\cdot}003321T^3 - 0{\cdot}00005102T^4$, in which $p$ represents the pressure in international atmospheres. Further measurements of the vapour pressure in the neighbourhood of the boiling point have given for this 20·39° (abs.). This value is 0·04° lower than the value obtained in a previous series of measurements. H. M. D.

**The Saturated Vapour Pressures of Octa-atomic Substances.** E. ARIÈS (*Compt. rend.*, 1918, **167**, 118—122).—The formula derived for the saturated vapour pressures of octa-atomic compounds is $\Pi = \tau^{29/10}Z/x$, where

$$x = [1 + (1 - \tau)(0{\cdot}88 - \tau)/\{0{\cdot}8 + (1 - \tau)^2\}]\tau^{19/10}.$$

The values, observed and calculated, are in fairly close agreement in the cases of methyl formate, ethyl bromide, and ethyl chloride, but in the cases of acetic acid and ethane it is not possible to obtain satisfactory verifications. W. G.

**Ebullioscopic Determinations with a Common Thermometer.** C. C. KIPLINGER (*J. Amer. Chem. Soc.*, 1918, **40**, 1020—1023).—An arrangement is described whereby an ordinary thermometer having a solid stem graduated in degrees may be read to hundredths of a degree with an error not exceeding 1%. A meter rod graduated in mm. is attached to a stand and equipped with a sliding peep-sight made from a strip of thin sheet metal. This rod is set parallel with the thermometer, the hole of the peep-sight being at a distance of 6 inches from the thermometer scale. The thermometer is fitted with a pen-shaped metallic indicator tapered to a width at the point equal to the apparent width of the capillary. The indicator is blackened, bent so that the tip is at a distance of 3 mm. from the scale, and attached to the thermometer by a screw clamp. The position of the mercury meniscus with reference to the nearest scale division is determined as follows. For clearness of explanation, let the meniscus be denoted by the letter *P*, the nearest scale division by *D*, and the tip of the indicator by *A*. Light is projected by a mirror on to the meniscus. The sliding peep-sight is moved until the scale division *D* is just hidden behind the tip *A* of the indicator; if the position of the peep-sight on the rod is denoted by *X*, then *XAD* is a straight line. The peep-sight is then moved to a position *Y* in which the gleam of the meniscus *P* is just hidden behind the tip *A*. The position of the meniscus *P* with reference to *D* is thus determined by the angle *XAY*; the distance *XY* once known, the apparatus may be dismantled, set up again, and the position of *P* with reference to *D* as definitely fixed as before, provided the indicator has not been moved relatively to the scale mark *D*.

In using the apparatus to determine molecular weights ebullioscopically, the principle adopted is to vary the concentration of the solute under examination until the rise of the b. p. is exactly the same as that produced by a substance of known molecular weight. For example, about 30 grams of carbon tetrachloride (constant 48) are placed in the weighed boiling tube with a known amount of borneol. When the temperature has become constant, the angle *XAY*, expressed in terms of divisions of the mm. scale, is determined as above, thus establishing the point *P*. The barometer is read, and the tube and its contents are weighed to determine the true weight of the solvent. Knowing the weight of the solvent and of the solute, and the molecular weight of the latter, the rise of the b. p. is calculated. The apparatus is cleaned and weighed, and a weighed amount of the substance of unknown molecular weight is added, together with a few grams of solvent. The solution is brought to the b. p., and small portions of solvent are added from time to time until the meniscus reaches the same point as in the borneol trial, as determined by the angle *XAY*. If too much solvent has been added, the condenser may be detached to allow some of the solvent to evaporate. When the adjustment is correct, the tube and its contents are weighed to ascertain the weight of the solvent. The rise of the b. p. is known from the borneol trial, hence the molecular weight can be calculated. In both cases, the same point *D* on the thermometer has been used for reference, hence a calibrated thermometer is unnecessary. The height of the flame must be kept constant throughout the work.

Molecular weights (the average of a series of determinations) determined in this manner compare favourably with those obtained by the usual method. C. S.

**A Laboratory Apparatus for Distilling in [Superheated] Steam under Reduced Pressure.** C. Harries and Reinold Haarmann (*Ber.*, 1918, **51**, 788—790).—Steam at 3—4 atmos. pressure is admitted through a throttle-valve into a superheating chamber maintained at about 300°, and then into the substance in the exhausted distilling flask, the neck of which is filled, by a simple device, with small pieces of glass rod in order to break up froth and prevent spirting. The apparatus is completely described with illustrations, and it is claimed that substances otherwise very non-volatile can be purified easily by distillation in this way, and hygroscopic salts deprived of solvent water. J. C. W.

**Definitions of Explosive Substance, Explosive Action, and Thermite.** Hans Schimank (*Zeitsch. Elektrochem.*, 1918, **24**, 213—214).—An explosive substance is defined as a substance which undergoes a very rapid exothermic change with the formation of gaseous products. Explosive action is differentiated from such actions as occur in overheated steam boilers. Thermite is a system which is capable of undergoing rapid exothermic reaction without the formation of gaseous products. J. F. S.

**Connexion between the Atomic Weights, Densities, and Heats of Reaction of the Elements.** Karl Fehrle (*Physikal. Zeitsch.*, 1918, **19**, 281—286).—A theoretical paper in which the author derives an expression for the heat of formation of a compound which involves only the atomic weights of the reacting elements and the densities of the elements and the compound formed. H. M. D.

**Thermal Properties of Sulphuric Acid and Oleum.** Alfred W. Porter (*Trans. Faraday Soc.*, 1918, **13**, 373—399).—The thermal data bearing on the concentration of sulphuric acid by evaporation have not hitherto been determined by experiment, and in view of the technical importance of the quantities in question, the author has attempted to supply the requisite information by indirect methods involving thermodynamical relations. The thermal data for the ordinary temperature are utilised in conjunction with calculations which give the variation of the heats of solution and dilution with temperature, and from these results the heats of total evaporation of water from sulphuric acid solutions at different temperatures are derived. A method of graphical representation, which facilitates the determination of the thermal data which may be required in a particular case, is described.

In the second part of the paper, similar methods are employed in the calculation of the thermal data for oleum (fuming sulphuric acid), and in particular of the heats of total evaporation or condensation of sulphur trioxide vapour for sulphuric acids containing 80—90% of sulphur trioxide. H. M. D.

**Experimental Determination of the Fictitious Heat of Solution.** ERNST COHEN and H. R. BRUINS (*Zeitsch. physikal. Chem.*, 1918, **93**, 43—58).—By the term fictitious heat of solution is to be understood the heat change which occurs when 1 gram-molecule of a substance at a measured temperature and pressure dissolves in an unlimited amount of its own saturated solution at the same temperature and pressure. Four methods of determining this value are described, and of these two have been used to determine the value for cadmium iodide in water. To measure the fictitious heat of solution of a salt $KA$, two galvanic elements, $XY$, are connected so as to oppose one another, and the resulting $E.M.F.$ is measured.

| $X$. | | | $Y$. | | |
|---|---|---|---|---|---|
| Electrode reversible with respect to $K$. | Saturated solution of $KA$ without solid phase. | Electrode reversible with respect to $A$. | Electrode reversible with respect to $A$. | Very dilute solution of $KA$. | Electrode reversible with respect to $K$. |

According to the Gibbs-Helmholtz equation, $E_c = n\epsilon(E_c - T.dE/dT)0{\cdot}2389$ gram cal., where $E_c$ is the $E.M.F.$ and $E_c$ the chemical energy of the double cell; also $E_c = W - F$, where $F$ is the fictitious heat of solution and $W$ the heat of solution of the dilute solution of $KA$. Consequently, $F = W - n\epsilon(E_c - T.dE/dT)$ gives the value of $F$.

In the second method, the combination

| | | | |
|---|---|---|---|
| Electrode reversible with respect to $K$. | Saturated solution of $KA$ without solid phase. | Dilute solution of $KA$. | Electrode reversible with respect to $K$ |

is measured, and from the equation $F = W - n/n_1 . \epsilon(E_c - T.dE/dT)0{\cdot}2389$ gram cal., the heat of solution is obtained; the symbols have the same meaning as before; $n_1$ is the number of gram ions transported from the saturated solution to the dilute solution by the passage of $\epsilon = 96{,}494$ coulombs. This method is complicated by the contact potential existing at the boundary of the two solutions.

The third method consists in measuring the $E.M.F.$ and temperature coefficient of the cell $X$ and of the same cell with solid phase $X_1$, and then using the equation of the same kind as those given above, the value of $F$ follows. A series of $E.M.F.$ determinations of these cells has been made at 16°, 18°, 20°, 22°, and 24°, and the temperature coefficient calculated for the case of cadmium iodide and the value $-1246$ gram cal. determined at 18°.

The fourth method depends on the measurements made in the last method; the relationship

$$(dE/dT)_X = (dE/dT)_{X1} + (dE/dC)_T . (dC/dT)$$

exists between the temperature coefficients of $X$ and $X_1$; $dC/dT$ is the temperature coefficient of the solubility, by substitution $F=[T.(dE/dC)_T.(dC/dT)]46,105$ gram cal. Hence to determine $F$, the values of $(dE/dC)_T$ and $(dC/dT)$ have to be determined.

These measurements have been made for cadmium iodide; the solubility of cadmium iodide is expressed by the equation $C=44{\cdot}18+0{\cdot}0828t+0{\cdot}000183t^2$, consequently $(dC/dT)_{18}=+0{\cdot}08939$. To ascertain the value of $dE/dC$, the *E.M.F.* of a number of elements $Cd/CdI_2\|$ of different concentrations have been measured at 18°, whence the dependence of the *E.M.F.* on concentration is given by the equation $E_{18}=0{\cdot}43150+0{\cdot}000283C-0{\cdot}00001428C^2$, so that $(dE/dC)_{18}=-0{\cdot}001023$ volt per cent. Using these values, $F=-1227$ gram cal. at 18°. J. F. S.

**Relative Volume Change which occurs on Mixing two Chemically Indifferent Gases, and its Measurement by Refraction of Light.** PAUL FUCHS (*Zeitsch. physikal. Chem.*, 1819, **92**, 641—676).—The change in total volume on mixing two chemically indifferent gases has been determined over the whole range of mixtures for the pairs nitrous oxide–nitrogen, carbon dioxide–nitrogen, oxygen–nitrogen, nitrous oxide–carbon dioxide, nitrous oxide–oxygen, oxygen–carbon dioxide by means of refraction measurements. The Haber-Löwe interferometer was used for this purpose, and the measurements were made at ordinary temperature and pressure. In every case, there is an increase in volume on mixing which is greater the more the two components differ in their physical behaviour. The volume change does not correspond with the ratio in which the gases are mixed, but reaches a maximum at a point beyond the equal concentration point in the sense that the maximum change lies with mixtures containing more than 50% of the gas of smaller critical temperature. The maximum volume change lies nearer to the 1:1 mixture the more the components resemble one another. The van der Waals's expression, $\Delta v=x(1-x)[\{a_1+a_2-2a_1a_2\}/MRT-\{b_1+b_2-2b_1b_2\}]$, was tested by means of the data obtained and found to be qualitatively in accord with the general results, but not strictly quantitatively correct. The dispersion of the gaseous mixtures is markedly different from that of the sum of the two components.

J. F. S.

**The Vapour Pressure of Dissociating Substances and the Volatilisation of Ammonia.** RUD. WEGSCHEIDER (*Zeitsch. anorg. Chem.*, 1918, **103**, 207—220).—An expression has been evolved for calculating the vapour pressure curves of dissociating substances, particularly those which on volatilisation dissociate partly into two molecules. The data required for the calculation are: the specific heats of solid (or liquid) and of dissociated and undissociated vapour; the heat of evaporation without dissociation and the heat of dissociation for each temperature; the dissociation constant and the vapour pressure for one temperature. The expression is used to examine the probability of different explanations put forward to account for the two vapour pressure curves of ammonium chloride. This substance is dimorphous, with a transition point at 184·5°, but the dimorphism will not account for the form of the curves unless the heat of transformation is at least −3000 cal., whereas the observed value is only −1030 cal. The assumption of further polymorphism with a second transition point either above or below 184·5° is shown to be invalid. The possibility is not excluded, however, that the ordinary form of ammonium chloride is labile, changing into the stable form only at high temperatures in presence of moisture. When perfectly dry, this labile form volatilises without dissociation, and its vapour pressure must be greater than the partial pressure of the undissociated molecules in the vapour of the stable form. An alternative explanation of the contradictory results sometimes obtained is that, whilst the ordinary form of ammonium chloride is stable, at times a labile form is obtained which when dry volatilises unchanged. E. H. R.

**The Principles of Diffusion, their Analogies and Applications.** Horace T. Brown (T., 1918, **113**, 559—585).—A lecture delivered before the Chemical Society on June 6th, 1918. D. F. T.

**Condition of Double Salts in Aqueous Solution.** D. Merrill Torrance and Nicholas Knight (*Chem. News*, 1918, **117**, 270—272. Compare Maxwell, A., 1917, ii, 562).—The changes occurring in the diffusion of solutions prepared from sodium aluminium sulphate, copper potassium sulphate, copper ammonium sulphate, magnesium ammonium sulphate, and potassium chromium sulphate have been examined at different temperatures and at different concentrations. The results indicate that the double salts are largely dissociated into the respective simple salts. The relative rates of diffusion appear to be influenced appreciably by ionic hydration. H. M. D.

**Hydrogen Ion and Hydrogen Bound to Ionogens: Chemistry of Electrolytic Dissociation.** A. Hantzsch (*Zeitsch. Elektrochem.*, 1918, **24**, 201—213).—A theoretical paper in which the intramolecular change involved in the formation of pseudo-acids is discussed. In this connexion, the position and method of linking of the hydrogen atom are considered, and theories put forward to explain the behaviour of the hydrogen in the different positions. The author proposes to substitute for the optical method of determining constitution the action of the substance in question on diazo-esters. The pseudo-acid is without action on the diazo-ester, whereas the true acid liberates nitrogen freely. A modification of the processes generally held to be occurring in ionisation is discussed. J. F. S.

**Liquid Crystals.** Tarini Charan Chaudhari (*Chem. News*, 1918, **117**, 269—270).—For closely related compounds, the intervals of temperature over which the liquid crystalline phase is stable appear to be simply related. Smits's dynamic theory of polymorphism in its application to liquid crystalline forms is considered to be unsatisfactory. There appears to be no definite connexion between the constitution of compounds and their capacity to form liquid crystals, and the author advances the view that the formation of such crystals is a general property of organic substances which melt without decomposition. H. M. D.

**Non-molecular Structure of Solids.** Arthur H. Compton (*J. Franklin Inst.*, 1918, **185**, 745—774).—The fact that the *X*-ray examination of certain simple crystals has shown that these have a non-molecular structure, suggests that this may be characteristic of all solid substances. In support of this hypothesis, a number of arguments are put forward, and the conclusion is drawn that in the solid state of aggregation the atoms are so intimately intermingled that particular molecules cannot be said to have any real existence.

The dependence of crystal form on chemical composition, *X*-ray observations, and considerations relative to the law of Dulong and Petit and the nature of cohesion, all suggest that the atoms of a crystalline solid oscillate about a mean position of stable equilibrium, and a comparison of the nature of cohesive forces with those which are concerned in chemical combination indicates that these are of the same nature and of the same order of magnitude. In this connexion, it is pointed out that there is a close parallelism between the melting temperatures and the "atomic heats of formation" for a large number of different substances. The melting point may be supposed to afford an approximate measure of the firmness with which the molecules are held together in the solid substance, whilst the "atomic heat of formation," obtained by dividing the molecular heat of formation by the number of atoms in the molecule, may be supposed to measure the intensity of the intramolecular forces.

Although certain properties of solid matter have been explained on the assumption that the ultimate atoms are definitely grouped into molecules, the author shows that recent work tends to replace the older methods of explanation by others in which no such assumption of molecular structure is specifically involved.

H. M. D.

**Connexion between Colour and Degree of Dispersity.** F. Kirchhof (*Kolloid Zeitsch.*, 1918, **22**, 98—102).—The view that the colour of disperse systems is determined by the size of the colloidal particles is considered in reference to the colours of the alkali metal sols and the changes which accompany the alteration in the valency of metal ions and the formation of complex ions. The relations exhibited suggest that the colour is fundamentally connected with the size of the disperse particles, whether these are atomic, ionic, or colloidal in nature. H. M. D.

**[Time Reactions in Colloidal Systems.]** D. VORLÄNDER (*Kolloid Zeitsch.*, 1918, **22**, 103—104).—According to Reitstötter (this vol., ii, 102), a solution of potassium ferrocyanide which has been used to bring about the coagulation of colloidal aluminium hydroxide gives no blue colour on the addition of a very dilute solution of a ferric salt. In the author's opinion, the apparent absence of a reaction is to be attributed to the fact that the reaction between ferrocyanide and ferric salt is a relatively slow one, the slow rate being determined by the colloidal nature of the ferric salt solution. Salts, acids, and other substances have a considerable influence on the speed of the reaction.

The reaction between ferricyanide and ferrous salt, on the other hand, takes place instantaneously, and in this system no colloidal particles are involved. A similar difference between the speeds of corresponding reactions is found in the action of hydrogen sulphide on stannic and stannous salts. In the case of the stannous salts, the ionic reactants give rise to an immediate precipitation of the metal sulphide. H. M. D.

**Rhythmic Diffusion Structures in Gelatin-Salt Jellies. II.** W. MOELLER (*Kolloid Zeitsch.*, 1918, **22**, 155—163. Compare A., 1917, ii, 410).—If drops of hydrochloric acid are allowed to fall on to a semi-liquid gelatin jelly containing sodium chloride, the semi-liquid condition being produced by suitably adjusting the temperature to which the previously cooled jelly is raised, diffusion of the acid takes place with the formation of well-developed spherites which resemble closely the spheritic structures that are found in plant cells. The formation of these spherites in the diffusion of the acid through the salt-jelly is interpreted in terms of the theory of jelly structure which has been put forward in previous papers. H. M. D.

**Coagulation of Roughly Dispersed Gold Hydrosols.** ARNE WESTGREN and J. REITSTÖTTER (*Zeitsch. physikal. Chem.*, 1918, **92**, 750—762).—The velocity of coagulation of gold hydrosols with large diameters has been determined in the following manner. To a quantity of the sol sufficient sodium chloride solution was added to produce rapid coagulation; after measured intervals of time, 10 c.c. of the mixture were withdrawn and stabilised by the addition of gelatin, and the number of non-coagulated particles was counted. Seven series of measurements were carried out, and from the results it is shown that the theory of Smoluchowski (A., 1917, ii, 297) on the process of coagulation is fully confirmed. The radius of attraction of the particles is slightly more than twice the radius of the particles themselves, which indicates that the particles must almost touch before they unite. J. F. S.

**Equilibrium of the Ternary System: Water, Sodium Sulphate, and Ammonium Sulphate.** CAMILLE MATIGNON and FERNAND MEYER (*Ann. Chim.*, 1918, [ix], **9**, 251—292).—A full account of work already published (compare this vol., ii, 66, 67).

W. G.

**Velocity of the Reaction between Nitric Oxide and Oxygen.** M. BODENSTEIN (*Zeitsch. Elektrochem.*, 1918, **24**, 183—201 *).—With the object of settling the controversy between Lunge and Berl and Raschig on the oxidation of nitric oxide in the lead chamber, the author has determined the velocity of oxidation of nitric oxide by oxygen. The two gases were mixed at temperatures from 0° to 90° and at low pressures, and the rate of change was followed by the decrease of pressure. The reaction proceeds strictly according to the equation for reactions of the third order, $dx/dt = kC_{O_2}C^2_{NO}$, and the velocity falls considerably with increase in temperature. The velocity is not affected by the addition of nitrogen peroxide, sulphur dioxide, or water vapour. From this it is argued that the oxidation of sulphur dioxide is not catalysed by oxides of nitrogen. The experimental results of Lunge and Berl, suitably recalculated, agree very well with the present work, and those of Raschig agree fairly well beyond the point where 50% of change has occurred. The experimental methods employed by Lunge and Raschig are discussed in the light of the present knowledge of the solubilities of the higher oxides of nitrogen. From this discussion, it is shown that nitric oxide and nitrogen peroxide exist in a constant equilibrium with nitrogen trioxide, which is destroyed with great rapidity in the presence of alkali hydroxide or concentrated sulphuric acid. It is shown that only those results dealing with changes above 50%, obtained by the methods of Raschig and Lunge, are trustworthy and usable. Consequently, the view of Raschig, that nitric oxide is rapidly oxidised to the trioxide, which is then slowly oxidised to the peroxide, is no longer tenable.

J. F. S.

**Velocity of Oxidation of Nitric Oxide.** E. BRINER and E. FRIDÖRI (*Helvetica Chim. Acta*, 1918, **1**, 181—185).—The kinetics of the oxidation of nitric oxide have been studied. Mixtures of oxygen and nitric oxide in proportions in which they occur in the production of nitric acid from the atmosphere have been allowed to pass along a series of tubes at constant temperature, and fitted with a series of taps whereby the gases could be removed at various points. The gaseous product was divided into two portions, one condensable by an alcohol–carbon dioxide refrigerant and the other by liquid air. It is shown that if the concentration of the oxygen is regarded as constant, the reaction is of the second order, but if the oxygen concentration is considered, the reaction corresponds with one of the third order and follows the equation $dx/dt = kC_{O_2}C^2_{NO}$. With regard to the influence of temperature on the reaction, it is shown that over the interval 0° to 60°, lowering the temperature 10° increases the velocity 10—20%.

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* and *Zeitsch. angew. Chem.*, 1918, **31**, I, 145—148.

J. F. S.

**The Saponification of Fats,** J. P. Treub (*J. Chim. phys.*, 1918, **16**, 107—174).—A résumé of work already published (compare A., 1917, ii, 528; this vol., ii, 71). W. G.

**Influence of Foreign Substances on the Activity of Catalysts. IV. Experiments with Palladium Hydrosol in the Presence of Mercury and Mercuric Oxide.** C. Paal and Wilhelm Hartmann (*Ber.*, 1918, **51**, 711—737).—In the course of many experiments on the catalysis of mixtures of hydrogen and oxygen by colloidal palladium or platinum, it has been observed that the catalyst becomes more or less passive in time if the gases are kept over mercury, and that, in all cases, if the catalyst remains in contact with mercury, it soon becomes quite inactive, even for the hydrogenation of nitro-compounds and unsaturated substances. Consequently, the authors have made an exhaustive study of the influence of ordinary and colloidal mercury and mercuric oxide on the catalysis of hydrogen and oxygen, and a few experiments on hydrogenations by palladium hydrosol.

The results show that palladium hydrosol has a remarkable power of converting mercury and mercuric oxide into colloidal solution, the oxide much more readily, whereby the palladium permanently loses its power of activating hydrogen, and thus catalysing processes of reduction, but does not suffer as a catalyst of hydrogen peroxide. It may be that a palladium–amalgam hydrosol is formed.

The sodium protalbinate used as a protection to the palladium hydrosol has no influence of itself on mercury. It is the colloidal palladium which causes these to enter the colloidal state. This protective colloid does, however, "peptisate" mercuric oxide in an atmosphere of hydrogen. J. C. W.

**Atomic Structure and Röntgen Spectra. I.** A. Sommerfeld (*Physikal. Zeitsch.*, 1918, **19**, 297—307).—A theoretical paper in which the arrangement of the rings of electrons in the atoms is discussed on a mathematical basis. H. M. D.

**The First and Second Electron Rings of the Atoms.** Jan Kroo (*Physikal. Zeitsch.*, 1918, **19**, 307—311).—On the assumption that the high-frequency lines in the $K_a$ series are due to the displacement of a single electron between rings which correspond respectively with one and two quanta, it is shown that experimental observations are consistent with the view that the former contains three electrons and the latter eight. H. M. D.

**The Atomic Theory. X. Space-filling Numbers and the Scale of Corresponding States.** Richard Lorenz (*Zeitsch. anorg. Chem.*, 1918, **103**, 243—248).—A formula has been deduced from which the mean value of the space-filling number of any substance, in the solid or liquid state, can be calculated. If $\phi$ be the ionic volume calculated from the ionic mobility and $V$ the volume derived from density determinations or by Kopp's formula, the space-filling number is given by $\phi/V$ (compare A., 1916, ii, 311, 312). For a variety of ions, the space-filling number $\phi/V_0$ referred to absolute zero on the empirical scale of corresponding states has a mean value of 0·4668. It is shown that the relation between volume and temperature can be expressed by an equation of the form $V/V_s = a . T/T_s + b$, where $s$ denotes the boiling point. From this it follows that $\phi/V = \phi/V_s(a . T/T_s + b)$. For solids, $a = 0·214$, $b = 0·709$, and for liquids $a = 0·453$, $b = 0·546$. Since $\phi/V_0 = 0·4668$, and $V_0/V_s$ has a mean value $= 0·709$, $\phi/V_s = 0·331$. Hence $\phi/V = 0·331/a . T/T_s + b$. An equation of state is thus derived in which the space-filling number appears as a function of temperature. E. H. R.

**Atomic Structure on the Basis of Atomic Disintegration and its Relationship to Chemical Linking, to Chemical Valency, and to the Electrochemical Character of the Elements.** EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1918, **93**, 1—42).—The author describes a theory of the structure of the atoms built up on the radioactive theory; by means of this theory, he explains the existence of atomic weights which differ from whole numbers by the assertion that such atomic weights are due to the presence of isotopes in the material examined. The abnormalities of the periodic system are explained in the same way; for example, iodine and tellurium are both mixtures of two isotopes of atomic mass 126 and 128 respectively, but in different quantities. The position of the triads of group VIII of the periodic system is explained as due to the similarity of the positive charge with dissimilarity of the masses of the middle zone and different stability of the exterior electron system. On the basis of this relationship, the author draws relationships between the structure of the atom and the valency and method of linking, to the change in valency, dissociation, and the electric charge of the atom, and to the relationship between the electrochemical character and the valency of the elements. The tendency of certain elements to act with one valency in preference to another is also considered. For details of these points, the original must be consulted. J. F. S.

**The Definition of the Term "Chemical Element."** RUD. WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1918, **92**, 741—749).—A theoretical discussion based on the definition of an element put forward by Paneth (A., 1916, ii, 240). It is asserted that this definition in no way corresponds with that of most chemists, who retain the old definition as sufficient to express the chemical idea of an element. J. F. S.

**Definition of the Term "Chemical Element."** FRITZ PANETH (*Zeitsch. physikal. Chem.*, 1918, **93**, 86—88).—An answer to Wegscheider's criticism (see preceding abstract) of the author's paper on this subject (A., 1916, ii, 240). J. F. S.

**Tables of Elements and Atoms.** FRITZ PANETH (*Zeitsch. physikal. Chem.*, 1918, **92**, 677—684).—The author proposes to substitute the present atomic weight table by two tables, (1) a table of combining weights containing those elements of which no isotopes exist, and using as combining weights the experimentally determined atomic weight, and (2) an atom table containing the whole of the elements, including all the isotopes with their theoretical atomic weights. The reasons for the proposed change are threefold: (1) There are more kinds of atoms than elements, (2) the combining weight of some elements is not the same as the atomic weight, and (3) in many cases there is no experimental confirmation of perfectly sound atomic weights which have been deduced from theoretical considerations. J. F. S.

**Twenty-fifth Annual Report of the Committee on Atomic Weights. Determinations Published during 1917.** GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1918, **40**, 1009—1014).—These comprise hydrogen, helium, carbon and sulphur, bromine, zirconium, tellurium, and samarium. Only in the case of zirconium has evidence been presented during the past year which seems to demand an important alteration in the previously accepted atomic weight. By conversion of the tetrachloride into the dioxide, Venable and Bell have obtained the value 91·76 for the atomic weight of zirconium (A., 1917, ii, 479). which is more than a unit higher than the value given by the International Committee on Atomic Weights. C. S.

**The Periodic System and Genesis of the Elements.** CURT SCHMIDT (*Zeitsch. anorg. Chem.*, 1918, **103**, 79—118).—The author's hypothesis of the genesis of the elements (A., 1911, ii, 198) has been considerably amplified. The elements do not belong to a single system, but to four partial systems genetically connected. The primary or hydrogen system is only represented by hydrogen, which is regarded as the sole survivor of a past evolutionary period of matter. In it, the metallic and metalloid properties of matter have not become differentiated. Baur, from a study of logarithmic atomic volume curves, drew the conclusion that two different generations of elements can be distinguished (A., 1911, ii, 480). These two generations practically correspond with the author's secondary or helium partial system, comprising the elements He–Ti, As–Zr, Sb–Ce, Bi–Th, and the tertiary or iron system, comprising the remainder of the elements, with the exception of the rare earth metals, which form a distinct quaternary system. When this hypothesis is adopted, the problem of the double periodicity of the elements disappears; for instance, the metals copper, silver, and gold no longer appear in the same group as the alkali metals, since the former belong to the tertiary, the latter to the secondary partial system. The inert gases appear as the central group of the He system with valency $=0$, contravalency $=\pm 8$, whilst the iron, palladium, and platinum triplets occupy a corresponding position in the tertiary system, with maximum valency $=\pm 8$, contravalency $=0$. The three blank spaces with which the He system begins are identified with elements detected spectroscopically in the nebulæ and the hottest fixed stars. These, with their probable atomic weights, are nebulium, the parent of nitrogen, Nu, 1·31 or 1·63; ekaoxygen, Eo, 2·36; and ekafluorine, Ef, 2·95.

Two principles are postulated, according to which the elements have probably been evolved: (1) the ontogenetic principle, involving the formation of the primary members of the different groups by direct condensation of protyl; (2) the phytogenetic principle, by which the higher members of the groups are developed from the lower by a process of integration. Evolution has taken place, not horizontally through the series, but vertically through the groups, each member of a horizontal series being independent of its neighbours. It follows that the atomic weights of potassium and argon, and of tellurium and iodine, present no anomaly. Some hitherto puzzling stellar phenomena also find their explanation in these principles; for instance, the occurrence of calcium and magnesium in certain stars which do not reveal the presence of oxygen and other elements of low atomic weight. The hypothesis is also in agreement with the relative abundance and distribution of the elements on the earth, and explains the frequent occurrence together of consecutive elements of the same group, such as zinc and cadmium. The direction of evolution was certainly from simpler to higher forms, following the course of cosmic evolution, and it is probable that, in atomic as in biological evolution, a process of selection with the survival of the fittest has been operative. There have probably been formed from time to time elements which, not being adaptable to the prevailing cosmic conditions, have undergone transformation. The radioactive elements are probably examples of such unsuitable types, and are at present passing through an evolutionary stage.

A rational system of nomenclature for the radioactive elements and their degradation products is suggested. Radium emanation is given the name *Radon*, Ro, which at once indicates its origin and its relationship to the argon group. The other emanations become *Thoron*, To, and *Acton*, Ao, respectively. The other degradation products are given names indicative of their derivation, manner of formation, and of the group of isotopes to which they are related. Thus radium-*D* becomes *β-radiotrilead*, with the symbol $\beta$-Ro$'''$Pb, and radium-$C_2$ becomes *β-radiotrithallium*, $\beta'$-Ro$'''$Tl, the accented $\beta$ indicating that the product does not belong to the principal radium series, but to a side-chain. A complete list of new names for all the known products from uranium, actinium, and thorium is given. E. H. R.

**New Table of the Periodic System.** Ingo W. D. Hackh (*J. Amer. Chem. Soc.*, 1918, **40**, 1023—1026).—Arranged in vertical rows on either side of the central column of the non-valent elements are, on the right-hand side, the elements of the groups IA, 2A, 3A, and 4 in the upper half of the table, and those of groups 1B, 2B, 3B, and 4 in the lower half, and, on the left-hand side, the elements of the groups 7A, 6A, 5A, and 4 in the upper half, and those of 7B, 6B, 5B, and 4 in the lower half. The elements of group 8 appear in the middle of the lower half of the table. This arrangement of the elements shows (1) a sharp classification of the elements into non-metals, noble gases, light metals, and heavy metals; (2) only five gaps, indicating that only five elements remain to be discovered; (3) elements having high electro-potential, simple spectra, and colourless ions appear in the upper half of the table, whilst those having low electro-potential, complex spectra, coloured ions, and tendency to form complex salts appear in the lower half; (4) on the left side of the table are the electronegative elements, those of the upper half forming strong acids, those of the lower half weak oxy-acids; on the right side of the table are the electropositive elements; (5) the middle of the lower half of the table is occupied by the amphoteric elements.

A peculiarity of the table is that the similarity of the elements is in the vertical direction in the upper half of the table and in the horizontal direction in the lower half. C. S.

**Progress of Chemistry during the Past One Hundred Years.** HORACE L. WELLS and HARRY W. FOOTE (*Amer. J. Sci.*, 1918, [iv], **46**, 259—302).—A brief account is given of the general lines of development of chemical knowledge during the last hundred years. H. M. D.

**New Filters.** R. ZSIGMONDY and W. BACHMANN (*Zeitsch. anorg. Chem.*, 1918, **103**, 119—128).—A new type of filter is described, termed a membrane filter, prepared by drying, under conditions not specified, solutions of certain colloids. The membranes thus obtained have a parchment-like appearance and a smooth surface, and are strong and durable. They can be prepared of any desired thickness and with any desired size of pore. The filters are very rapid in action and are particularly suitable for vacuum filtration, as they will stand high pressures. The membrane chosen for any particular filtration should be such that the pores are smaller than the diameter of the particles to be filtered. Under these conditions, no adsorption takes place, the pores do not get choked, and the membrane can be washed and used again with undiminished filtration velocity. A filter which, under 70 cm. pressure and with an area of 80 sq. cm. will pass 100 c.c. of water in eight seconds (an 8 sec. filter), will filter completely a graphite sol in which the particles are 200—300 $\mu\mu$ in diameter. A similar membrane will also stop gold particles of 80—100 $\mu\mu$, but allows particles 30—40 $\mu\mu$ to pass through.

The membranes can also be used for separating the constituents of a mixed colloidal solution. Thus when a solution containing

Prussian blue and benzopurpurine was filtered through a 5 sec. filter (a relatively coarse membrane), the former was stopped completely, whilst the latter passed through. This was collected completely on a 3 min. filter. It is anticipated that the new filters will be valuable for many laboratory and technical purposes.

E. H. R.

## Inorganic Chemistry.

**The Influence of Different Modifications of Sulphur on the Melting Point of Sulphur.** ERNST BECKMANN, RUDOLF PAUL, and OTTO LIESCHE (*Zeitsch. anorg. Chem.*, 1918, **103**, 189—206). —The "natural freezing point" of sulphur, 114·5°, is 4·75° below that of normal sulphur, $S_\lambda$. Assuming that the depression of the freezing point is due to the presence of $S_\pi = 128$, the cryoscopic constant of sulphur being 213 (this vol., ii, 218), the proportion of $S_\pi$ present must be 2·78%. This is in good agreement with Aten's conclusions, but not with that of Smith and his co-workers, who decided that "natural" sulphur contains about 3·6% of amorphous sulphur, $S_\mu$. The conclusion that "natural" sulphur does not contain $S_\mu$ is also supported by the results of experiments on the effect of the addition of various forms of sulphur to sulphur of f. p. 114·5°, the additions being made to samples, prepared under standard conditions, at a temperature just above the melting point. Amorphous sulphur, prepared in a variety of ways, has practically no effect on the freezing point, and is shown to be rapidly transformed into a mixture of $S_\lambda$ and $S_\pi$ of the same composition as the fused mass. If the fusion is rapidly cooled after the addition of the $S_\mu$, only about 24% of the added sulphur is still insoluble in carbon disulphide. When added to a fused mass having a lower f. p. than 114·5°, $S_\mu$ has no effect, but when added to one having a higher f. p., it has the effect of lowering it towards the "natural" f. p., indicating that at the higher temperature relatively more $S_\pi$ is formed from the $S_\mu$.

When $S_\mu$ is heated, it shows no sharp melting point, but, having reached 120°, it has at once the "natural" freezing point 114·5°. If a mixture of rhombic sulphur with about 5% $S_\mu$ is melted, it has a freezing point about 2° lower than that of a sample of rhombic sulphur similarly treated, indicating that under these conditions the $S_\mu$ decomposes into 23% $S_\pi$ and 77% $S_\lambda$.

A sample of $S_\pi$ prepared according to Aten's method (A., 1915, ii, 254) when added to a sample of "natural" sulphur lowered the f. p. slightly, indicating, however, only about 4·6% $S_\pi$ in the preparation. Both rhombic and monoclinic sulphur raise the f. p. of "natural" sulphur by increasing the proportion of $S_\lambda$.

A sample of Engel's sulphur, $S_\rho$, having a molecular weight of

192, was found to lower the f. p. of natural sulphur, but owing to the rapidity with which it decomposes, only 73% of the calculated depression could be observed. The decomposition of this form of sulphur is not a simple unimolecular reaction, and $S_\mu$ appears to be an intermediate product. E. H. R.

**Flame Reactions.** JACOB PAPISH (*J. Physical Chem.*, 1918, **22**, 430—432).—When the vapour of selenium dioxide is introduced into a Bunsen flame, an intense blue colour is produced. Elementary selenium is deposited on a cold surface which is brought into the blue flame. In similar circumstances, the vapour of tellurium dioxide produces a blue-coloured flame tinged with green in its uppermost part, and a bright, metallic mirror is deposited on a cold surface held in the hottest part of the flame. The reduction of the oxides in the flame is supposed to be the cause of the characteristic luminescence. H. M. D.

**Occurrence of Hydrogen Selenide in Rain and Snow.** TH. GASSMANN (*Helvetica Chim. Acta*, 1918, **1**, 52—54).—One hundred c.c. of rain are concentrated to 80 c.c., and a strong current of sulphur dioxide is passed through the liquid for fifteen minutes. On keeping over night, a reddish-brown precipitate forms, which is shown to be selenium in the following way. It is oxidised with aqua regia and the solution precipitated with hydrogen sulphide; the precipitate is dissolved in fuming nitric acid, and the selenium precipitated either by hydrochloric acid or stannous chloride. Snow may be similarly treated.

Selenium may also be detected by precipitating the concentrated rain or snow water with a concentrated solution of barium chloride. The precipitate is collected after keeping over night, washed with ether, and dried in a desiccator over soda-lime. On treatment with concentrated hydrochloric acid, hydrogen selenide is evolved, which blackens a lead acetate paper.

It is probable that hydrogen selenide is not present as such in the rain or snow, but is in combination with a second component which has not yet been identified. T. S. P.

**A New Oxide of Selenium.** FRITZ VON KONEK (*Ber.*, 1918, **51**, 872—876).—When diantipyryl selenoselenide, $R_2Se{:}Se$ (this vol., i, 407), was burnt in a bomb in oxygen under 25—30 atm. pressure, with the idea of converting the selenium into selenic acid, a white, amorphous deposit was found adhering firmly to the walls of the crucible. This proved to be an *oxide*, approximating to the formula $Se_3O_4$, which is almost insoluble in water, and is decomposed by boiling sodium hydroxide, about one-third of the selenium being deposited in the free state, the remainder giving rise to sodium salts of selenium acids. Strange to say, diantipyryl monoselenide, and diselenides of the type R·Se·Se·R, provided by Lesser (A., 1912, i, 642) and Bauer (A., 1913, i, 263), gave no trace of this oxide. J. C. W.

**Nitrogen Chloride, with a Convenient Method for its Preparation.** Hashmat Rai (*Chem. News*, 1918, **117**, 253).—About 10 c.c. of a freshly prepared, filtered, concentrated solution of bleaching powder in a large test-tube are cooled in ice to about 0°, and an equal volume of cold, saturated ammonium chloride solution is added. When the vigorous reaction has subsided, after ten minutes, the nitrogen chloride is exploded by the addition of turpentine. The chloride on the surface explodes instantly, that at the bottom more violently after some time, the interval between the two explosions depending on the height of the liquid column, the amount of turpentine added, the nature of the surface explosion, and the amount of nitrogen chloride present. All apparatus must be absolutely free from grease and direct sunlight should be entirely excluded. C. S.

**Catalytic and Thermal Syntheses of Ammonia.** E. B. Maxted (*J. Soc. Chem. Ind.*, 1918, **37**, 232—235T).—The author discusses the effect of the time of contact, temperature, and pressure on the percentage of ammonia formed and on the yield per litre of catalyst space in connexion with the catalytic synthesis of ammonia. Experiments are described on the thermal synthesis of ammonia at arc temperatures. J. F. S.

**Determination of the Surface Tension and Critical Density of Ammonia.** Alfred Berthoud (*Helvetica Chim. Acta*, 1918, **1**, 84—87).—The critical density of anhydrous ammonia has been determined by Young's method, as modified by Ter-Gazarian, the densities of the liquid and vapour being measured between 0° and the critical temperature, 132·3°. The critical density ($d_c$) is found to be 0·2362, whereas the calculated value, ($d_{th}$), assuming that the gas laws hold up to the critical point, is 0·05609. The ratio of $d_c$ to $d_{th}$ is 4·211, whereas the value of this ratio for normal liquids is approximately 3·6. This indicates that ammonia is associated even at the critical point, and the association is confirmed by measurements of the surface tension; $K$, in the Eötvös-Ramsay formula, is found to be 1·80 between 11° and 59°, giving a value of 1·27 for the association factor. Trouton's rule also gives a value of 23·8, which is higher than the normal value for unassociated liquids. T. S. P.

**Reduction of the Oxides of Nitrogen to Ammonia. Stability of Nitric Oxide.** Ph. A. Guye and Fritz Schneider (*Helvetica Chim. Acta*, 1918, **1**, 33—52).—In Switzerland, the conditions are such that oxides of nitrogen can be manufactured more conveniently than ammonia, so that a knowledge of the conditions under which the former are reduced to the latter becomes necessary. The authors have carried out such an investigation, using a special apparatus in which known mixtures of hydrogen with the respective oxides of nitrogen were passed over heated reduced nickel as catalyst. The ammonia formed was estimated by absorption in a known volume of standard sulphuric acid. In some cases, this estimation was controlled by heating the solution with excess of sodium hydroxide and again absorbing the ammonia in standard acid; this was necessary in the case of nitrogen peroxide, since some ammonium nitrate is forming during the reduction.

In order to be quite certain of the results obtained, it was necessary to carry out preliminary experiments on the action of heat alone on some of the oxides of nitrogen used, since the statements found in the literature on this subject are somewhat contradictory and often have reference to the results obtained when the gas is heated under pressure. An apparatus was used in which the gas could be heated under atmospheric pressure, since the experiments on reduction were carried out at this pressure. It consisted of a cylindrical glass bulb heated in an electric furnace. Sealed on to the bottom of the bulb was a narrow glass tube, which could be cooled in liquid air or other cooling medium; products such as nitrogen peroxide could then be frozen out and identified.

In order to decompose nitric oxide under atmospheric pressure, it is necessary to raise the temperature to 575° and keep it there for several hours, even in the presence of spongy platinum as catalyst. Under these conditions, and contrary to what takes place under pressure, there is no formation of nitrous oxide. The primary products of decomposition are nitrogen and oxygen; on cooling, the oxygen reacts with undecomposed nitric oxide to give nitrogen peroxide. Nitrous oxide decomposes simply into nitrogen and oxygen.

In the reduction of the oxides $NO$, $N_2O$, and $NO_2$ by hydrogen, with nickel as catalyst, two reactions take place simultaneously, the one giving ammonia and the other nitrogen; for example, $2NO + 5H_2 = 2NH_3 + 2H_2O$, $2NO + H_2 = N_2 + H_2O$. Both in the reduction of nitric oxide and of nitrogen peroxide, the formation of intermediate products, namely, nitrous oxide and nitric oxide respectively, does not occur.

In all these reactions, the condition of the reduced nickel plays an important part, and two different preparations do not necessarily give the same results. Also there is an optimum yield of ammonia which depends on the composition of the gaseous mixture and on the velocity with which the gases are circulated over the nickel.

Temperatures of 250—300° appear to be the best for the formation of ammonia. Below these temperatures, the reduction takes place slowly, whilst above these temperatures, the nickel gradually loses its activity and the ammonia is appreciably decomposed into its elements.

Nitric oxide gives the best yields, 70% of the gas, on an average, being transformed into ammonia; 25—39% of nitrogen peroxide and only 3—7% of nitrous oxide is reduced to ammonia.

The reduction of the oxides of nitrogen to ammonia does not therefore appear to be an advantageous process from the manufacturing point of view, except perhaps in the case of nitric oxide, where a more systematic study of the conditions may give better results. T. S. P.

**The Revision of the Atomic Weight of Carbon from the Densities of Acetylene, Ethylene, and Ethane.** Knut Stahrfoss (*J. Chim. phys.*, 1918, **16**, 175—200).—The values obtained for the weight of a normal litre of gas are: for acetylene, 1·1791 grams; for ethylene, 1·2610 grams; for ethane, 1·3565 grams. From these, the atomic weight of carbon is calculated as 12·00, but this value will be subject to revision when it has been possible to determine directly the departure from Avogadro's law in the case of these gases, and when new determinations of the density of ethylene have been made. W. G.

**Ultra-microscopic Investigation of very thin Metal Films obtained by Evaporation in High Vacuum. II.** W. Reinders and L. Hamburger (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1135—1154. Compare A., 1917, ii, 405).—The thin films of metal which are deposited on a glass surface when various metals are strongly heated in a highly exhausted space have been examined according to the method previously described (*loc. cit.*). It is found that elements which melt at high temperatures, such as tungsten, molybdenum, platinum, nickel, iron, and carbon, give rise to films which under the ultra-microscope are either entirely or for the most part devoid of structure. Elements of lower melting point show, on the other hand, a tendency to form films which have a clearly recognisable structure with ultra-microns as the structural units. The elements belonging to this group which have been examined are silver, gold, copper, magnesium, zinc, and cadmium. When the temperature of the glass surface on which the metal vapours condense was cooled by means of liquid air, the silver, copper, and gold films obtained were similar to those of the elements of high melting point in the first group. The lowering of the temperature of the condensing surface did not, however, eliminate the structural characteristics from the films of magnesium, zinc, and cadmium, although the coarseness of the structure was considerably reduced. The films devoid of structure show distinct signs of heterogeneity when the temperature is raised, this effect being very clearly marked in the case of films of silver, gold, platinum, iron, and molybdenum.

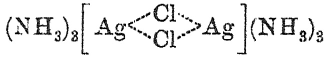
The films produced by tungsten, molybdenum, platinum, nickel, and iron are colourless, whilst those obtained from the other metals examined are coloured. That this colour does not depend on the structure or absence of structure is shown by the fact that the films of copper, silver, and gold have the same colour, whether these films are structureless or are ultra-microscopically heterogeneous. The colour effect is consequently due to the selective absorption of the atoms and is a characteristic property of the metal. H. M. D.

**A Complete Review of Solutions of Oceanic Salts. IV.** Ernst Jänecke (*Zeitsch. anorg. Chem.*, 1918, **103**, 1—54. Compare this vol., ii, 70).—The influence of temperature on the equilibrium of the system $(Na_2-K_2-Mg)(Cl_2-SO_4)$ is given a graphic representation by the method developed in previous papers. The numerous diagrams given are fully explained in the paper.

E. H. R.

**The Nature of Subsidiary Valencies. XIX. Ammines of Silver.** Fritz Ephraim (*Ber.*, 1918, **51**, 706—710).—The vapour tensions of the triammines of some silver salts have been measured by the author's usual method. A few of the compounds had only recently been prepared by Bruni and Levi (A., 1916, ii, 482), whilst others had long been known. The following list gives the temperatures at which the vapour tensions of the triammines are 760 mm.: perchlorate, 79·5°; chlorate, 65·5° (by extrapolation; highest reading, 51·5°); chloride, 17·7°; bromide, 3·7°; bromate, 1°; permanganate, 12°; nitrate, 63°; nitrite, 69·3°. The iodide, iodate, and periodate form no triammines.

When the acid radicle is truly anionic, it is usually found that the stability of the ammines rises from chlorides to iodides and from chlorates to iodates. The complete reversal of this order in the case of the silver salts suggests, therefore, that there is a complex cation present, at any rate in the solid compounds, as expressed, for example, in the formula



$$(NH_3)_3\left[Ag\begin{matrix}<Cl>\\<Cl>\end{matrix}Ag\right](NH_3)_3$$

J. C. W.

**The Crystal Form of Barium Iodide Hexahydrate.** O. Mügge (*Centr. Min.*, 1918, 105—107).—Commercial barium iodide crystallises at the ordinary temperature in large, hexagonal prisms without distinct end faces. The crystals are apparently isomorphous with $SrCl_2,6H_2O$. The prism faces show diagonal striation always in the same direction on all faces of all crystals. The crystal class is probably trapezohedral tetartohedral; $a : c = 1 : 0·538$ (approx.); double refraction fairly strong, negative. The crystals melt in their water of crystallisation at 25·7°. E. H. R.

**Double Carbonates of Sodium and Potassium with the Heavy Metals.** Malcolm Percival Applebey and Kenneth Westmacott Lane (T., 1918, **113**, 609—622).—An examination of the preparation and properties of the double salts

$Na_2Cu(CO_3)_2,3H_2O$,

$Na_2Co(CO_3)_2,4H_2O$, and $K_2Co(CO_3)_2,4H_2O$ (compare Deville, *Ann. Chim. Phys.*, 1851, [iii], **33**, 75; Reynolds, T., 1898, **73**, 262; Gröger, A., 1907, ii, 240; Wood and Jones, A., 1907, ii, 620; Luther and Kršnjavi, A., 1905, ii, 705). The solubility equilibria are investigated for the sodium–copper and potassium–cobalt salts in the additional presence of the corresponding alkali hydrogen carbonate, this being necessary in order to reduce the tendency to the separation of basic compounds.

For experimental details, reference should be made to the original. D. F. T.

**Utilisation of Waste Nessler Solution.** WILLIAM CLIFFORD (*J. Soc. Chem. Ind.*, 1918, **37**, 179T).—Nessler solution residues are treated with a few c.c. of sulphuric acid, whereby the mercuric iodide is precipitated. The mercuric iodide may be converted into sodium iodide as follows: 200 grams of the iodide are placed with 500 c.c. of water in a litre flask, and 20 grams of iron filings added. The mixture is heated for sixty minutes on a water-bath, when the reaction is complete, mercury being precipitated and ferrous iodide formed in solution. The green solution obtained by filtration is boiled and kept overnight, when it becomes ruby-red. The iron is then precipitated by sodium carbonate or hydroxide. Generally a second precipitation is necessary to remove all the iron. The filtrates from the second precipitation may be used directly for oxygen absorption determinations. Nessler solution may be prepared with sodium iodide and hydroxide just as well as with the potassium compounds. J. F. S.

**Ceric Oxychloride, produced in the Electrolysis of Cerous Chloride.** HANS ARNOLD (*Zeitsch. Elektrochem.*, 1918, **24**, 137—138).—When molten cerous chloride is electrolysed, a secondary reaction occurs at about 900° as long as there is an excess of water present in the molten mass. The product of this secondary reaction is a dark brown, amorphous powder which is deposited on the cooler parts of the anode. The product is very hygroscopic, and on analysis is shown to be a mixture of ammonium chloride, ceric oxychloride, and water. All attempts to remove the ammonium chloride by washing or sublimation converted the basic ceric chloride into cerous chloride. It is suggested that the product is produced from ceric chloride, formed on the anode, by the action of water, thus: $CeCl_4 + H_2O = CeOCl_2 + 2HCl$. The product always contains water, and analysis indicates that the water is combined and is present as $CeOCl_2,10H_2O$. The compound is highly deliquescent and is hydrolysed by water with the formation of ceric hydroxide and cerous chloride. J. F. S.

**Carbides.** OTTO RUFF (*Zeitsch. Elektrochem.*, 1918, **24**, 157—162).—A preliminary paper on the temperature of formation and the stability range of carbides. The present paper deals with the equilibria between carbon and aluminium and between chromium and carbon. Aluminium carbide, $Al_4C_3$, sublimes at temperatures up to 2200° without melting and with some decomposition. This decomposition is independent of temperature. The melting point of aluminium carbide lies above this temperature. A vapour pressure curve has been constructed up to 2300°. At 2200°, aluminium carbide is in equilibrium with graphite, aluminium saturated with graphite and vapour under a pressure of 400 mm. In the case of chromium and carbon, a composition-temperature diagram has been constructed for the pressure 10 mm. At 2270°, the mixture boils, and the vapour consists entirely of chromium. Between 2050° and 2250°, the fusion remains constant in composition and corresponds with $Cr_3C_2$. Below 2050° down to 1875°, graphite and the carbide, $Cr_3C_2$, exist side by side as solid phases. The compound $Cr_5C_2$ is also shown to exist. J. F. S.

**The Determination of the Crystal Structure of Complex Compounds.** PAUL NIGGLI (*Physikal Zeitsch.*, 1918, **19**, 225—234).—The point system characteristic of any crystal can be determined from a knowledge of the crystal class and of the ratios of the distances between successive reflecting planes of atoms in the crystal in different directions as determined by the $X$-ray reflection method. As an example, the case of potassium alum, already examined by Vegard and Schjelderup (this vol., ii, 156), is worked out. The point system is the one designated $T_h^2$, and the elementary cube contains four molecules of the form $[Al(H_4O_2)_6](SO_4)_2K$. The aluminium, potassium, and sulphur atoms can be immediately identified with appropriate points in the point system. The oxygen atoms of the $SO_4$ group appear to be of two kinds, three being alike, distributed symmetrically about a trigonal axis, the fourth being situated on the trigonal axis, and the four together forming a trigonal pyramid with the sulphur atom at the centre. The oxygen atoms of the water molecules probably correspond with two distinct groups of unfixed points in the system. The exact positions of the sulphur and oxygen points are not fixed by the symmetry of the system, but equations are developed by means of which their co-ordinates may be calculated when the relative intensities of the $X$-ray reflection spectra of different orders are known for the faces (100), (110), and (111). The author's solution of the alum structure differs to some extent from that put forward by Vegard and Schjelderup in the disposition of the oxygen atoms. E. H. R.

**Crystal Structure of the Alums and the Rôle of the Water of Crystallisation.** CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik*, 1918, [iv], **55**, 397—400).—Polemical. The authors point out that the results of Vegard and Schjelderup (this vol., ii, 156) on the rôle of the water of crystallisation in the building up of the space grating of alums are not new, but were published by them in an earlier paper (A., 1916, ii, 505). A criticism of the spacial model of alums put forward by the same authors concludes the paper. J. F. S.

**Basic Exchange in Permutite. I.** V. ROTHMUND and G. KORNFELD (*Zeitsch. anorg. Chem.*, 1918, **103**, 129—163).—The basic exchange which takes place between a hydrated aluminosilicate such as permutite (compare Gans, A., 1914, ii, 55) and a neutral salt solution is to be regarded as a true chemical change and not as an adsorption phenomenon as suggested by Wiegner (A., 1912, ii, 981). In the case of permutite, an equilibrium rapidly becomes established with the solution. The resulting mixed permutite functions as a single solid phase, and is to be regarded as a solid solution, the composition of which depends on the relative concentrations of the cations in the solution. In the case of univalent cations, the composition of the permutite is independent of the total concentration of the solution, but when bivalent cations, for example, calcium, are present, the total as well as the relative concentration must be taken into account. The experimental work was confined to univalent metals, the equilibrium between silver permutite and the nitrates of potassium, rubidium, lithium, ammonium, and thallium, and between sodium permutite and ammonium and thallium nitrates, being investigated. If $c_1$ and $c_2$ represent the concentration of two bases in solution, and $c'_1$ and $c'_2$ their concentrations in the permutite in equilibrium with the solution, the empirical relation found is $c'_1/c'_2 \cdot (c_2/c_1)^{\beta} = K$, in which $\beta$ is less than unity. The values of $\beta$ and $K$ vary considerably in the different cases examined. A bibliography of the subject of basic exchange is appended to the paper. E. H. R.

**Place of Manganese in the Periodic System.** F. Russell von Bichowsky (*J. Amer. Chem. Soc.*, 1918, **40**, 1040—1046).—The arguments usually given for placing manganese in the seventh group are based on the periodic law, isomorphism, and chemical properties, and appear open to question in the light of modern knowledge. On the other hand, twelve different lines of argument based on purely chemical relationships are given by the author for placing manganese in the eighth group with iron, nickel, and cobalt. Moreover, the atom colours of the various valences of manganese show that the normal valence must be even, not odd (Bichowsky, this vol., ii, 142).

An improved form of the periodic table is presented showing the relations of the eighth and the rare earth groups to the rest of the periodic system. C. S.

**Structure of Tungsten Steels and the Change under Heat Treatment.** Kôtarô Honda and Takejirô Murakami (*Sci. Rep. Tohôku Imp. Univ.*, 1918, **6**, 235—283).—Tungsten steels containing 0·12 to 1·57% of carbon and 0·23 to 30·0% of tungsten have been systematically investigated in respect of their magnetic susceptibility and micro-structure, and attention has been paid to the change of structure at high temperatures.

According to microscopic observations, the system iron–tungsten is characterised by the formation of a single compound, $Fe_2W$. The tungsten in tungsten steels may be present either in the form of iron tungstide or tungsten carbide, WC, or in both forms. The tungstide is soluble in iron to an extent represented by 9% of tungsten, and in steels which contain a larger proportion of tungsten than corresponds with this limiting value the tungstide is present as a separate phase in globular form. As the carbon content increases, a larger proportion of tungsten is required for the appearance of the globules, this fact being due to the formation of tungsten carbide.

In the normal condition, the tungsten carbide is present in the form of the double carbide, $4Fe_3C,WC$, which decomposes at 400°. At high temperatures, tungsten carbide reacts with iron in accordance with the equation $WC+5Fe=Fe_3C+Fe_2W$, and when the steel is subsequently cooled, the transformation points are lowered by the dissolving of the iron tungstide in the iron.

The changes which occur under the influence of various methods of heat treatment are described in reference to a large number of magnetic susceptibility curves and photomicrographs. The authors consider that the occurrence of the double carbide, $4Fe_3C,WC$, has been clearly proved by their investigations. H. M. D.

**Adsorption Compounds. Ferriarsenites.** TADEUSZ ORYNG (*Kolloid Zeitsch.*, 1918, **22**, 149—154).—When a solution of a ferric salt is mixed with a solution of sodium arsenite and sodium hydroxide added to the mixture, a precipitate is obtained which contains ferric and arsenious oxides, and this has been regarded as an adsorption compound, the arsenious oxide being adsorbed by the precipitated ferric hydroxide. The systematic investigation of the composition of the precipitate in relation to that of the mother liquor has led the author to the conclusion that the facts cannot be satisfactorily explained in terms of the adsorption theory, and that the precipitate consists of a mixture of definite chemical compounds represented by the general formula $xFe(OH)_3,yAs_2O_3'''$. In the author's opinion, many supposed cases of adsorption are probably examples of chemical changes of a similar type.

H. M. D.

**Peptisation of Ferric Arsenate and Phosphate and Formation of their Gels.** HARRY N. HOLMES and ROSSLEENE ARNOLD (*J. Amer. Chem. Soc.*, 1918, **40**, 1014—1019).—A continuation of previous work (Holmes and Rindfusz, A., 1916, ii, 624). It is now found that unwashed precipitates of ferric arsenate or phosphate are stabilised by any soluble arsenates or phosphates that may be present, and therefore much more concentrated alkali hydroxide may be used as peptising agent, and it may be added more rapidly and in greater excess. The presence of thoroughly adsorbed alkali arsenate in precipitated ferric arsenate compels the use of more sodium hydroxide for peptisation, but the resulting colloid is stable in direct proportion to the amount of alkali arsenate present. Furthermore, if it is ammonium arsenate that is present in excess, less base is required for peptisation than in the case of other alkali arsenates, the order being $NH_4$, K, Na, Li. Ferric arsenate or phosphate can be peptised by sodium hydroxide or ferric chloride.

With sodium hydroxide, the action is greatly aided by sucrose or glycerol, but is hindered by sodium chloride. On dialysis of the colloids formed by the action of sodium hydroxide on ferric arsenate or phosphate, no gels form except in the presence of sucrose or glycerol.

Dialysis of the colloids formed by the ferric chloride peptisation of ferric arsenate or phosphate yields excellent gels. With barely enough ferric chloride for complete peptisation, the gels are opalescent and yellowish-grey, forming in a few days. With an excess of ferric chloride, the gels are red, weaker in structure, and slower in formation in direct proportion to this excess. Gels form in much less time when the original precipitate of ferric arsenate contains thoroughly adsorbed alkali arsenate; this accelerating influence of alkali arsenates decreases in the order $NH_4 > K > Na > Li$.

C. S.

**Nitrosopentamminecobalt Salts.** A. WERNER and P. KARRER (*Helvetica Chim. Acta*, 1918, 1, 54—78).—Sand and Genssler (A., 1903, ii, 549; 1904, ii, 39) have described two series of salts which they obtained by the action of nitric oxide on ammoniacal solutions of cobalt salts; the one series was red and the other black in colour, and both corresponded with the formula $[NO{\cdot}Co(NH_3)_5]X_2$. It was considered that the two series were valency isomerides, and the present authors have taken up the question again in order further to investigate the question of valency. They find that Sand and Genssler's statements with respect to the black series are correct, and some new salts are described, of which the iodate is very stable; most of the statements with respect to the red series are found to be incorrect.

*Black Nitrosopentamminecobalt Salts.*—The chloride,

$$[NO{\cdot}Co(NH_3)_5]Cl_2,$$

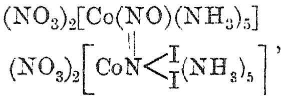
is obtained by the method described by Sand and Genssler. In stoppered bottles it is quite stable, but on exposure to the air transformation to the red salt takes place, accompanied by partial decomposition. The transformation is due to moisture, and is not dependent on the action of light. The nitrate and sulphate are very unstable and cannot be obtained pure. The *iodate*,

$$[NO{\cdot}Co(NH_3)_5](IO_3)_2,$$

is precipitated almost immediately when nitric oxide is passed through a strongly ammoniacal solution of cobalt iodate, air being carefully excluded during the operation. It forms a blackish-brown, crystalline powder, and is quite stable in the absence of moisture. Attempts to prepare the bromide, iodide, cyanide, and chlorate were unsuccessful.

*Dinitrosodecamminedicobalt Salts (Red Salts)*, $YX_4$, where $Y=[N_2O_2{\cdot}Co_2(NH_3)_{10}]$.—The nitrate, $Y(NO_3)_4$, is obtained by Sand and Genssler's method, but the yields are very variable. It is best purified by precipitation from aqueous solution with sodium nitrate. When 20—25% nitric acid is added to the aqueous solution, an orange-coloured precipitate of the *acid nitrate*, $Y(NO_3)_4,HNO_3,H_2O$, is formed, which readily loses its water of crystallisation over calcium chloride; over phosphoric oxide, some nitric acid also seems to be lost. The compound described by Sand and Genssler, namely, $[Y(NO_3)_4,2HNO_3]-H_2O$, does not exist, nor could the pure additive products of the nitrate with silver nitrate and lead nitrate, described by these authors, be obtained.

The *acid perchlorate*, $Y(ClO_4)_4,HClO_4,H_2O$, falls as a reddish-brown powder when the cold, concentrated solution of the nitrate is precipitated with 30% perchloric acid solution. The compound $[Y(ClO_4)_4,2HNO_3]-H_2O$ does not exist. The compound



$$\begin{array}{c}(NO_3)_2[Co(NO)(NH_3)_5]\\ \| \\ (NO_3)_2\left[CoN\Big\langle\begin{matrix}I\\I\end{matrix}(NH_3)_5\right]\end{array},$$

described by Sand and Genssler as being prepared by the action of potassium iodide and nitric acid on the nitrate could not be obtained. Probably a periodide is produced, which, however, is very unstable and cannot be obtained pure. By precipitation of a solution of the nitrate with potassium iodide, the *iodide*, $YI_4,4H_2O$, is obtained as a brownish-yellow, flocculent precipitate; it is only obtained pure after several reprecipitations with potassium iodide. The compound, $Y(NO_3)_2I_2,KI$, does not exist.

The double sulphate, $Y(SO_4)_2,[N_2O_2Co_2(NH_3)_9(OH_2)](SO_4)_2,2H_2O$, prepared by Sand and Genssler by the action of nitric oxide on an ammoniacal solution of cobalt sulphate, could not be obtained. The *sulphate*, $Y(SO_4)_2,2H_2O$, was obtained from the nitrate by the aid of nitron sulphate; after collecting the nitron nitrate, the filtrate is precipitated with alcohol and ether. The compound, $[Y(NO_3)_4,H_2SO_4]-H_2O$, described by Sand and Genssler, could not be obtained, but by interaction of nitron sulphate with the nitrate, the *acid sulphate*, $Y_2(SO_4)_4,H_2SO_4,4H_2O$, was prepared. The *bromide*, $YBr_4,3H_2O$, is prepared by an analogous method to that used for the iodide, whilst the *acid bromide*, $YBr_4,HBr,H_2O$, is obtained from the acid sulphate by the action of fuming hydrobromic acid. A chloride could not be obtained. Interaction of the nitrate and oxalic acid gave the *acid oxalate*,

$$Y(C_2O_4)_2,4H_2C_2O_4,3H_2O,$$

as yellowish-brown needles, which on trituration with concentrated ammonia gave the *oxalate*, $Y(C_2O_4)_2,H_2O$, as long, dark red needles. The salts $[(N_2O_2)_2Co_4(NH_3)_9H_2O](SO_4)_4,2H_2O$ and

$$[Co_3(N_2OC_2O_4)(NH_3)_9H_2O](C_2O_4H)_4$$

do not exist.

The *acid iodate*, $Y(IO_3)_4,4HIO_3$, and the *chromate*,

$$Y(CrO_4)_2,4H_2O,$$

are prepared from the nitrate by treatment with iodic acid and potassium chromate respectively. The former is a dark red, crystalline powder, and the latter an amorphous, yellowish-brown salt.

The above red nitrosopentamminecobalt salts must be considered as having the general formula $(N_2O_2)\Big\langle\begin{matrix}Co(NH_3)_5X_2\\Co(NH_3)_5X_2\end{matrix}$. Attempts to decide the nature of the radicle $N_2O_2$ have not yet met with success. By the action of acids, the radicle is split off as $N_2O_2H_2$, which, however, immediately decomposes, giving $N_2O$; the compound $N_2O_2H_2$ could not be isolated or shown to be in solution, and statements made by Sand and Genssler that it is present in the solution obtained by the action of 68% nitric acid on the red nitrate are not correct. Since the compound $H_2N_2O_2$ may be hyponitrous acid, attempts were made to synthesise the red salts by the action of silver hyponitrite on chloropentamminecobalt nitrate, but they were unsuccessful, aquopentamminecobalt salts being obtained. T. S. P.

**The Solubility of some Metallic Hydroxides in Water.** GUSTAV ALMKVIST (*Zeitsch. anorg. Chem.*, 1918, **103**, 240—242).—The solubilities of the hydroxides $Ni(OH)_2$, $Co(OH)_2$, $BiO(OH)$, $Fe(OH)_3$, and $MnO(OH)_2$ in water at 20° have been determined. As the results were required for analytical purposes, ordinary distilled water, not freed from carbon dioxide, was used. For the determination, the purified hydroxide was stirred for four days with water. About 2 litres of the filtrate were then evaporated to a small bulk, and the quantity dissolved was estimated gravimetrically, nickel and cobalt being weighed as sulphate after conversion of the hydroxide into sulphide, bismuth as $Bi_2O_3$. Iron and manganese, however, were determined colorimetrically. The following results were obtained per litre: $Ni(OH)_2$, 12·7 mg.; $Co(OH)_2$, 3·18 mg.; $BiO(OH)$, 1·44 mg.; $Fe(OH)_3$, 0·151 mg.; $MnO(OH)_2$, 0·43 mg. E. H. R.

**New Mixed Crystals and Compounds of Nickel Oxide with other Metallic Oxides.** J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1918, **103**, 249—252).—Experiments on the miscibility of nickel oxide with other oxides were made by fusing the mixed oxides together in varying proportions at about 900°, using potassium chloride as a flux. With magnesium oxide, homogeneous mixed crystals are formed within the limits 27—90% nickel oxide; outside these limits, it is difficult to distinguish microscopically between mixed crystals and the pure oxides. The mixed crystals are cubic and are intermediate in colour between the components.

With zinc oxide, homogeneous mixed crystals are formed when the zinc oxide is in excess. The crystals appear to be hexagonal, like those of Rinmann's Green. Probably a nickel zincate is formed which is miscible with excess of zinc oxide (compare A., 1914, ii, 133; 1916, ii, 331). The colours of mixed crystals of varying composition are not strictly proportional to their composition.

Homogeneous mixed crystals of nickel and manganese oxide were prepared with compositions ranging from $NiO,5MnO$ to $5NiO,MnO$. The crystals are slightly yellowish-green in colour and form octahedra and octahedral cubes.

Nickel oxide forms with alumina a blue compound, $NiO,Al_2O_3$, crystallising in small octahedra or octahedral cubes. Even a small excess of either oxide can readily be distinguished microscopically. The corresponding cobalt aluminate has been previously described (A., 1915, ii, 636).

With tin dioxide, nickel oxide reacts but slowly below 1000°, but a small quantity of a stannate analogous to cobalt stannate (A., 1915, ii, 638) appears to be formed. E. H. R.

**Colloidal Products of the Reactions between Potassium Dichromate and Stannous Salts.** J. C. WITT (*J. Amer. Chem. Soc.*, 1918, **40**, 1026—1030).—The phenomena observed when *N*-potassium dichromate is added to *N*-stannous chloride in equivalent proportions (Neidle and Witt, A., 1915, ii, 780; 1916, ii, 256; Neidle and Crombie, A., 1917, ii, 93) have been investigated. The mottled appearance is caused by a local excess of potassium dichromate; on keeping after the addition of an equivalent of dichromate, the remainder of the stannous chloride present gradually removed the dichromate from the precipitate, and the colloid was regenerated, producing a homogeneous, green liquid. A like precipitation of the colloids is produced by other electrolytes containing an anion having a valency greater than one. The reaction between stannous sulphate and potassium dichromate is essentially similar to that with the chloride. C. S.

**Zirconium Nitride.** P. BRUÈRE and ED. CHAUVENET (*Compt. rend.*, 1918, **167**, 201—203).—The authors have prepared zirconium nitride by heating the tetra-ammonia derivative of zirconium chloride, $ZrCl_4,4NH_3$, at 350°, and find that the product has the composition $Zr_3N_4$, and not $Zr_3N_8$ as given by Wöhler (compare *Annalen*, 1839, **48**, 94) or $Zr_2N_3$ as found by Mallet (*Amer. J. Sci.*, 1859, [ii], **28**, 346). The authors have repeated Wöhler's work, but are unable to confirm his formula. W. G.

**The Combinations of Acid Zirconyl Sulphate with some Alkali Sulphates (Na, NH$_4$).** ED. CHAUVENET and (MLLE.) H. GUEYLARD (*Compt. rend.*, 1918, **167**, 126—129. Compare this vol., ii, 269).—Thermochemical measurements indicate the existence of the following compounds of acid zirconyl sulphate with sodium sulphate and ammonium sulphate respectively:

$$2(ZrOSO_4,SO_3),3Na_2SO_4,$$
$$3(ZrOSO_4,SO_3),2Na_2SO_4,\ ZrOSO_4,SO_3,(NH_4)_2SO_4,$$
$$ZrOSO_4,SO_3,2(NH_4)_2SO_4,$$

to which correspond the following hydrates, which are stable in air at the ordinary temperature: $2(ZrOSO_4,SO_3),3Na_2SO_4,8H_2O$, $3(ZrOSO_4,SO_3),2Na_2SO_4,7H_2O$, and the trihydrate in the case of each of the double ammonium salts. Measurements have been made of the density, refractive index, and electrical conductivity of solutions of mixtures of varying proportions of the acid zirconyl sulphate and one of the alkali sulphates. In the case of mixtures with potassium sulphate, the formation of a precipitate prevented the making of exact measurements. W. G.

**Pure Antimony.** E. Groschuff (*Zeitsch. anorg. Chem.*, 1918, **103**, 164—188).—Technically refined antimony is purer than electrolytic antimony prepared by the electrolysis of antimony sulphide solutions. The latter product when further refined gives a metal of a high degree of purity, containing less than 0·02% impurity. The different methods for purifying antimony and antimony compounds are reviewed. For the production of chemically pure antimony, the following process has been adopted. Antimony trichloride or pentachloride is purified by distillation, and is then transformed into the chlorantimonic acid, $SbCl_6H,4\frac{1}{2}H_2O$, described by Weinland and Schmid (A., 1905, ii, 326). This compound is specially adapted to the separation of antimony from all likely metallic impurities. After purification by recrystallisation, the chlorantimonic acid is readily hydrolysed to antimonic acid, which is reduced to metal preferably by melting with potassium cyanide. In a large preparation (about a kilogram) purified in this way, no impurities at all could be detected by qualitative methods. The melting point of the pure antimony is 630·3°.

Methods for the qualitative and quantitative analysis of nominally pure antimony are given. The solution of the antimony is effected in a variety of ways, according to the impurities present. The antimony is then converted into chlorantimonic acid, which is fractionally crystallised. The impurities are concentrated in the mother liquors, which are combined and analysed by the usual methods. Pure antimony dissolves completely in red, fuming nitric acid without evolution of gas. Under certain conditions of precipitation, antimonic acid is obtained in a sparingly soluble modification. E. H. R.

**The Hydrates with $3H_2O$ or $n \times 3H_2O$.** Marcel Delépine and Pierre Boussi (*Bull. Soc. chim.*, 1918, [iv], **23**, 278—288).—A study of the dehydration of various platinichlorides, iridi- and irido-chlorides, and rhodochlorides containing 6 or $12H_2O$ does not support Rosenstiehl's views (compare A., 1911, ii, 270, 386) on polymerised water and water of crystallisation. W. G.

**The Acid Function of Osmium Tetroxide.** L. Tschugaev (*Compt. rend.*, 1918, **167**, 162—163).—That osmium tetroxide has an acid function is shown by the fact that it forms definite compounds with the alkali hydroxides. The *potassium* compound, $OsO_4,2KOH$, the *rubidium* compound, $OsO_4,RbOH$, and the two *cæsium* compounds, $OsO_4,CsOH$ and $2OsO_4,CsOH$, are all crystalline, of an orange or brown colour, and readily soluble in water, in which solution they are strongly hydrolysed. The *compound* $[Rh,4C_5H_5N,Cl_2]OH,2OsO_4$ was also obtained in the form of thin, yellow plates. W. G.

# Mineralogical Chemistry.

**Boron, Lithium, and Thallium in Volcanic Exhalations.** A. Brun (*Bull. Soc. franç. Min.*, 1917, **40**, 107—110).—These elements may very often be detected spectrographically in the saline sublimations of fumaroles and in the altered scoria of Vesuvius and other volcanoes. Thallium was detected from Vesuvius, Etna, and Teneriffe in amounts ranging from 2·5 to 24 in 10,000. It is present as the soluble chloride in association with ammonium and sodium chloride, or as an insoluble sulphide in association with sulphides of arsenic. L. J. S.

**Thallium in the Lead Sulpharsenate Minerals of the Binnenthal, Switzerland.** A. Brun (*Bull. Soc. franç. Min.*, 1917, **40**, 110—111).—Spectroscopic examination of crystals of sartorite, dufrenoysite, and jordanite, as well as all fragments giving a black or chocolate-brown streak, showed the presence of thallium. Hutchinsonite [which contains 5% of Tl] was not detected amongst these fragments. The association with sulphur and arsenic is here analogous to the Vesuvian occurrence. L. J. S.

**Minerals from the Stanley Antimony Mine, Idaho.** Earl V. Shannon (*Amer. Min.*, 1918, **3**, 23—27).—The ore consists of pure stibnite in a quartz-vein which carries some gold. The following mineral-species are described: stibnite, blende, gold, iron-pyrites, mispickel, kermesite, valentinite, cervantite, stibioferrite, and volgerite. The volgerite occurs abundantly as an earthy, dirty-white crust on stibnite; material from the interior of the crusts is more compact, somewhat translucent with a faint resinous lustre, and pale greyish-brown in colour. $D^{20}$ 3·082, H $3\frac{1}{2}$. The mineral is completely soluble in hot concentrated hydrochloric acid, and at a red heat it gives off some oxygen, the higher oxide, $Sb_2O_5$, apparently passing into $Sb_2O_4$. It contains $H_2O$ 12·6, $Fe_2O_3$ 1·4%. The amount of water is lower than that required by the usual formula ($Sb_2O_5,5H_2O$ or $Sb_2O_5,4H_2O$), but this may perhaps be explained by the colloidal nature of the material.
L. J. S.

**A peculiar Fibrous Form of Opal.** George P. Merrill (*Amer. Min.*, 1918, **3**, 11—12).—Bunches of light grey, asbestiform material are embedded in a massive mixture of opal and chalcedony from Metolius, Oregon. It has the appearance of serpentine-asbestos (chrysotile), but is brittle and is harsh to the touch. Under the microscope it is seen to consist of wavy, colourless, isotropic fibres. Analysis gave: $SiO_2$ 89·56, $Al_2O_3+Fe_2O_3$ 4·72; loss on ignition, 5·62%. L. J. S.

**Ores of Manganese and Iron from the Crystalline Massif of Brosteni, Roumania.** V. C. BUTUREANU (*Bull. Soc. franç. Min.*, 1917, **40**, 164—177).—A résumé is given of previous papers (P. Poni, A., 1901, ii, 26; Butureanu, A., 1908, ii, 955; 1909, ii, 745; 1912, ii, 949). The minerals considered are manganites of manganese and iron (brostenites of Poni) and carbonates of manganese and iron (ponites of Butureanu). The brostenites have been derived by the alteration of the ponites. Numerous analyses are quoted showing the wide range in composition. L. J. S.

**Ulexite from Lang, California.** WILLIAM FOSHAG (*Amer. Min.*, 1918, **3**, 35).—This occurs in some quantity, associated with colemanite, howlite, and calcite, in the Sterling Borax Co. mine. It has a fibrous structure with a botryoidal surface; it differs from the ordinary type of this mineral in being more compact and harder ($H=3\frac{1}{2}$) and in its association with colemanite. Analysis gave:

| $B_2O_3$. | CaO. | $H_2O$. | $Na_2O$. | Total. |
|---|---|---|---|---|
| 43·13 | 14·14 | 35·68 | [7·05] | 100·00 |

The mineral is probably a lake deposit from the alkaline waters of the neighbouring streams, and the colemanite has perhaps been derived from it by the action of alkaline chloride solutions.

L. J. S.

**Randannite [ = Diatomite] from Madagascar.** A. LACROIX (*Bull. Soc. franç. Min.*, 1916, **39**, 85—88).—A bed of diatomite, interbedded with basaltic tuffs, is exposed on the banks of the stream Sandrangoty, near Mt. Raynaud, in the extreme north of Madagascar. The material is white, porous, and fairly coherent. Under the microscope, the material is seen to be colourless, colloidal, and to be composed of fusiform diatoms. Analysis by Raoult gave:

| $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MgO. | CaO. |
|---|---|---|---|---|---|---|
| 76·00 | 1·24 | 6·24 | 1·80 | 0·85 | 0·07 | 0·80 |

| $Na_2O$. | $K_2O$. | $P_2O_5$. | $H_2O$ at 105°. | $H_2O$ (ign.). | Organic matter. | Total. |
|---|---|---|---|---|---|---|
| 0·39 | 0·18 | 0·12 | 5·87 | 6·07 | 0·60 | 100·23 |

The high percentage of titanium dioxide suggests that the impurities ($Al_2O_3$ and $SiO_2$ [2·90%] insoluble in alkali) are due to the presence of admixed laterite. L. J. S.

**Lattice-like Inclusions in Calcite from North Burgess, Ontario.** R. P. D. GRAHAM (*Min. Mag.*, 1918, **18**, 252—258).—Pale blue, coarsely crystalline calcite from this locality shows twin-striations, due to repeated twinning on the obtuse negative rhombohedron *e*(110), and encloses fine needles, which are arranged parallel to the edges of this rhombohedron. On dissolving the calcite in acid, these needles remain as a delicate and intricate network or lattice-like structure. Analyses of this material, D 2·5, gave the results under I and I*a*, agreeing with the formula $5MgO,6SiO_2,4H_2O$. The material is slightly attacked by hydrochloric acid; after digestion with concentrated acid and drying at 100°, the residue had the composition given under II. The blue calcite itself (anal. III) contains very little magnesia.

| | $SiO_2$. | MgO. | FeO. | CaO. | $H_2O$. | $CO_2$. | Total. |
|---|---|---|---|---|---|---|---|
| I. | 57·23 | 30·35 | 1·66 | 0·37 | n.d. | — | — |
| IA. | 56·37 | 30·43 | 2·47 | nil | 10·87 | — | 100·14 |
| II. | 63·93 | 26·16 | 1·21 | — | 8·08 | — | 99·38 |
| III. | — | 0·41 | — | 56·12 | — | 43·53 | 100·06 |

L. J. S.

**Mineralogy of Black Lake Area, Quebec.** EUGENE POITEVIN and R. P. D. GRAHAM (*Museum Bull. Geol. Survey Canada*, 1918, No. 27, 1—82).—An account is given of thirty-four mineral species found in the several asbestos (chrysotile) and chromite mines and quarries in the 'serpentine belt' near Black Lake, Megantic Co., Quebec. Many of these minerals are alumino-silicates rich in lime, such as idocrase, grossularite, etc., which are usually formed by the contact-metamorphism of impure limestones. In this area, however, they occur as fillings in dyke-like fissures penetrating peridotite and serpentine, that is, in rocks containing very little lime (0·20—0·68% CaO). These dykes are considered to represent the last phase of the igneous intrusions, when the residual acid magma or magmatic waters became enriched in lime by their solvent action on the surrounding rocks. Analyses are given of the following minerals: I. Diopside, colourless crystals from the Montreal chrome pit. Corresponding with the low percentage of iron, the refractive indices ($\alpha_{Na}=1·669$, $\beta=1·676$, $\gamma=1·698$) are lower than any previously recorded for diopside. II. Grossularite, colourless, transparent crystals from Southwark pit; refractive index, 1·734. III., lilac-coloured, and IV., yellowish-green crystals of idocrase; the refractive indices ($\omega=1·708$; $\epsilon=1·705$) of the lilac-coloured crystals are low. V.—VII. *Colerainite*, a new species, forming minute, colourless, hexagonal scales which are optically uniaxial and positive ($n=1·56$), and are often aggregated as white rosettes or botryoidal forms. Analysis V of the crystals leads to the formula $4MgO,Al_2O_3,2SiO_2,5H_2O$. Analyses VI and VII are of the underlying matrix, which is white, finely granular to compact, and resembles unglazed porcelain in appearance; this material

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. |
|---|---|---|---|---|---|---|
| I. | 54·77 | — | 0·17 | 0·89 | 0·11 | 26·33 |
| II. | 39·49 | 22·35 | — | 1·00 | 0·15 | 36·62 |
| III. | 36·88 | 20·03 | 0·85 | n.d. | 0·23 | 37·61 |
| IV. | 36·62 | 15·96 | 4·30 | 0·54 | trace | 38·66 |
| V. | 24·40 | 22·77 | 0·45 | n.d. | 0·09 | 0·10 |
| VI. | 26·98 | 16·10 | 0·22 | nil | 0·20 | 0·12 |
| VII. | 33·00 | 13·12 | — | — | — | trace |
| VIII. | 43·31 | 0·38 | 0·27 | nil | trace | 0·12 |
| IX. | 50·29 | 6·23 | | 1·00 | — | nil |
| X. | 48·88 | 3·56 | | 1·36 | — | nil |

| | MgO. | $(K,Na)_2O$. | $H_2O$. | Total. | Sp. gr. |
|---|---|---|---|---|---|
| I. | 18·46 | — | — | 100·73 | 3·267 |
| II. | 0·28 | — | — | 99·89 | 3·60 |
| III. | 2·17 | — | 3·09 | 100·86 | 3·32 |
| IV. | 1·25 | — | 3·18 | 100·51 | — |
| V. | 32·70 | 0·30 | 19·63 | 100·44 | 2·51 |
| VI. | 36·56 | 0·28 | 19·91 | 100·37 | 2·44 |
| VII. | 35·30 | 0·26 | 18·67 | 100·35 | 2·34 |
| VIII. | 40·03 | 0·28 | 15·77 | 100·16 | 2·51 |
| IX. | 29·99 | — | 13·30 | 100·81 | — |
| X. | 31·41 | — | 15·67 | 100·88 | — |

consists mainly of the mineral colerainite. VIII is of 'precious' or 'noble' serpentine from the Megantic mine; this is chrysoprase-green and translucent with a somewhat waxy or greasy lustre. Included in it are sometimes grains and veins of chromite and the rare mineral stichtite, a chromiferous magnesium hydroxy-carbonate. IX and X are of porcellophite, an impure variety of serpentine; IX is of pale grey material from the Megantic mine, and X, of pale brown material from the Hall chrome pit; both are very compact, resembling dried clay in appearance, and so light that they float on water. L. J. S.

**Flokite, a New Zeolite from Iceland.** KAREN CALLISEN (*Medd. Dansk Geol. For.*, 1917, **5**, No. 9, 1—6).—A specimen in the Copenhagen Museum, labelled 'Eskefjord? Iceland,' and regarded as mesolite, proved on examination to represent a new species. It forms slender, flattened, monoclinic prisms with perfect (100) at (010) cleavages. The crystals are water-clear or pale yellowish-green. Sections perpendicular to the prism-zone show a division into sectors with different optical orientations. $\alpha_{Na} = 1·4720$, $\gamma_{Na} = 1·4736$; D 2·102; H 5. Before the blowpipe, the material fuses readily with intumescence; it is not attacked by hydrochloric acid. Analysis by C. Christensen gives the formula $H_8(Ca,Na_2)Al_2Si_9O_{26},2H_2O$.

| $SiO_2$. | $Al_2O_3$. | CaO. | MgO. | $Na_2O$. | $H_2O$ > 100°. | $H_2O$ < 100°. | Total. |
|---|---|---|---|---|---|---|---|
| 67·69 | 12·43 | 2·65 | 0·09 | 4·36 | 8·82 | 4·53 | 100·57 |

L. J. S.

**The Mesosiderite-Grahamite Group of Meteorites: Analysis of Vasca Muerta, Hainholz, Simondium, and Powder Mill Creek.** G. T. PRIOR (*Min. Mag.*, 1918, **18**, 151—172. Compare A., 1916, ii, 635).—In the Rose-Tschermak-Brezina classification of meteorites, the mesosiderites are defined as consisting of iron and crystalline olivine and bronzite, with the metallic and stony matter in approximately equal amounts, whilst the grahamites contain the same constituents with the addition of plagioclase-felspar. It is now found that typical members of both groups contain abundant felspar, and that there is no essential difference between them. For the combined group, the earlier name mesosiderite is retained. The members of this group consist mainly of pyroxene and felspar, with nickel-iron in large amount, but rather unevenly distributed, and nodules of olivine somewhat sparsely distributed, but occasionally of considerable size. Accessory constituents are troilite, chromite, and schreibersite. The felspar is nearly pure anorthite; the pyroxene is fairly rich in iron, the ratio of MgO : FeO being about 2 : 1; the olivine, on the other hand, is poor in iron, the ratio MgO : FeO being from 6 : 1 to 10 : 1; and the nickel-iron is poor in nickel, Fe : Ni = 10 : 1 to 13 : 1. The cataclastic structure of the mesosiderites suggests that they represent a mixture of two types, to one of which belong the pyroxene and anorthite, and to the other the iron and olivine.

Vaca Muerta (Chili).—Several masses ('Sierra de Choca,' 'Llano del Inca,' 'Doña Inez,' etc.) are included in this fall. The bulk-composition (I) is deduced from analyses of the magnetically attracted portion and of the portions soluble and insoluble in hydrochloric acid of the unattracted portion. I*a* is of the olivine, corresponding with $10Mg_2SiO_4,Fe_2SiO_4$. and I*b* is the mineral composition. Hainholz (Westphalia).—II the bulk-composition, II*a* of the olivine ($7Mg_2SiO_4,Fe_2SiO_4$), and II*b* the mineral composition. Simondium (Cape Colony) (A., 1910, ii, 315).—This is much weathered. The portion of the unattracted material soluble in water contained NiO 1·28, CaO 0·91, $SO_3$ 2·71%. Other detailed analyses are given. Powder Mill Creek (Tennessee).—The attracted portion contained Fe 73·15, Ni 5·61, insoluble 11·58, anorthite, etc. (9·66) = 100. The olivine gave III*a*, corresponding with $10Mg_2SiO_4.Fe_2SiO_4$. The composition of some other meteorites of this group is also discussed.

| | Nickel-iron. | | | Troilite. | | Schreibersite. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Fe. | Ni. | Co. | Fe. | S. | Fe. | Ni. | P. | $SiO_2$. | $Al_2O_3$ | $Fe_2O_3$. | $Cr_2O_3$. |
| I. | 38·25 | 2·90 | 0·36 | 1·37 | 0·79 | 1·27 | 0·70 | 0·35 | 26·02 | 5·87 | 1·36 | 0·45 |
| II. | 42·13 | 4·00 | 0·41 | 2·52 | 1·44 | 0·36 | 0·23 | 0·10 | 21·69 | 4·99 | 2·77 | 0·33 |

| | FeO. | MnO. | NiO. | CaO. | MgO. | $Na_2O$. | $P_2O_5$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 7·03 | 0·24 | — | 4·35 | 7·36 | 0·18 | — | 0·54 | 99·39 |
| II. | 6·19 | trace | 0·48 | 3·49 | 7·07 | 0·21 | 0·34 | 1·20 | 99·95 |

| | $SiO_2$. | FeO. | MgO. | Insol. | Total. |
|---|---|---|---|---|---|
| IA. | 39·89 | 8·98 | 49·50 | 1·95 | 100·32 |
| IIA. | 40·48 | 11·59 | 42·97 | 2·76 | 97·80 |
| IIIA. | 40·18 | 9·15 | 48·91 | 1·42 | 99·66 |

| | Nickel-iron. | Troilite. | Anorthite. | Pyroxene. |
|---|---|---|---|---|
| IB. | 41½ | 2 | 17 | 32 |
| IIB. | 46½ | 4 | 14½ | 27 |

| | Olivine. | Chromite. | Rust. | Schreibersite. |
|---|---|---|---|---|
| IB. | 1½ | 1 | 2 | 3 |
| IIB. | 1½ | ½ | 4 | 2 |

L. J. S.

**Composition of the Meteorites Amana and Eagle Station.** G. T. Prior (*Min. Mag.*, 1918, **18**, 173—179).—The Amana or Homestead meteoric stones, which fell in Iowa Co., Iowa, on

February 12th, 1875, were in the same year analysed by G. D. Hinrichs; J. L. Smith, and by C. W. Gümbel and Schwager. These analytical results show some discrepancies amongst themselves and are not in agreement with the author's theory of the genetic relationship of meteorites (A., 1916, ii, 635). The following new analysis was therefore made. The bulk-composition (I) deduced from analyses of the magnetically attracted portion and of the portions soluble and insoluble in hydrochloric acid of the unattracted portion, agrees with the following mineral composition: felspar 9·76, apatite 0·22, chromite 0·44, bronzite

$(4\frac{1}{2}MgSiO_3,FeSiO_3,\frac{1}{2}CaSiO_3)$

30·75, olivine $(3\frac{1}{2}Mg_2SiO_4,Fe_2SiO_4)$ 40·15, nickel-iron 10·99, troilite 6·25, water 0·47%. This meteorite therefore contains about 11% of nickel-iron in which the ratio of Fe : Ni is 8 : 1, whilst the ratio of MgO : FeO in the ferromagnesian silicates is 4 : 1; it thus occupies an intermediate position between the type-meteorites Cronstad (C2) and Baroti (C3).

| | Nickel-iron. | | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Fe. | Ni. | Co. | Fe. | S. | $SiO_2$. | $Al_2O_3$. | $Cr_2O_3$. | $Fe_2O_3$. |
| I. | 9·71 | 1·19 | 0·09 | 3·97 | 2·28 | 39·27 | 2·10 | 0·32 | 0·40 |
| | FeO. | MnO. | CaO. | MgO. | $Na_2O$. | $K_2O$. | $H_2O$. | $P_2O_5$. | Total. |
| I. | 12·06 | 0·08 | 1·78 | 24·88 | 0·92 | 0·13 | 0·47 | 0·26 | 99·91 |

A new analysis of the Eagle Station meteorite, which was found in 1880 in Carroll Co., Kentucky, gave II for the attracted portion and III for the olivine. These results confirm those of J. B. Mackintosh (1887). In the nickel-iron the ratio of Fe : Ni is about 6 : 1 (instead of more than 10 : 1, as in most other pallasites), and in the olivine the ratio of MgO : FeO is about 4 : 1 (instead of about 7 : 1). In composition, as well as in structure, this pallasite is thus exceptional; and it may perhaps be placed in the group A3 (A., 1916, ii, 635).

| | Fe. | Ni. | Co. | $SiO_2$. | MgO. | FeO. | P,S,&c. | Total. |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| II. | 79·74 | 13·98 | 1·04 | 1·42 | 1·74 | 0·77 | (1·31) | 100·00 |
| III. | — | — | — | 39·22 | 42·31 | 18·83 | — | 100·36 |

L. J. S.

## Analytical Chemistry.

**Quinone-Phenolate Theory of Indicators. Absorption Spectra of Solutions of Phenolsulphonephthalein and its Tetrabromo- and Tetranitro-derivatives and their Salts, and of Analogous Substances.** E. C. White and S. F. Acree (*J. Amer. Chem. Soc.*, 1918, **40**, 1092—1099).—Since phenolsulphonephthalein and its derivatives and their salts furnish the best series of indicators yet found for acidimetry and for the study of the quinone–phenolate theory (White, *Science*, 1915, **42**, 101; Lubs and Acree, A., 1917, ii, 97; Lubs and Clark, A., 1916, ii, 44, 570; White and Acree, A., 1917, i, 340), the authors intend to make a series of phenolsulphonethaleins covering a range of hydrogen-ion concentrations from $10^{-1}$ to $10^{-13}$ or more.

The following results are established in the present paper. The yellow colour and the absorption spectrum of phenolsulphonephthalein solutions are not altered by the addition of alkali hydroxide up to 0·75 mol. When more alkali is added, the yellow colour changes to deep red, and there is a corresponding shift in the absorption band. This is interpreted as evidence that the intense red colour of the alkali salts of indicators of this series does not come from the non-ionised quinone–phenol group, but arises from the quinone–phenolate anion. In accordance with this conception, it is found that the introduction of negative bromo- and nitro-groups into the phenol nucleus increases the ionisation of the phenol group, increases the conductivity, lowers the $P_H$ value, and gives to the solution a greater concentration of quinone–phenolate anions, and therefore increases the deep red colour and changes the position of the absorption band so as to cut out a part of the yellow. The addition of hydrochloric acid suppresses the ionisation of the phenol group and changes the deep red colour into the yellow of the quinone, and therefore shifts the absorption band so as to include less of the yellow.

The similarity of the absorption spectra of alkaline solutions of sulphonephthaleins, phenolphthaleins, aurin, fluorescein, and related substances gives evidence that the deep red colour in all these cases arises from the presence of a quinone–phenolate anion.

C. S.

**Behaviour and Detection of the smallest Quantities of Carbon Monoxide in the Chlorate Pipette.** K. A. Hofmann and Helge Schibsted (*Ber.*, 1918, **51**, 837—842. Compare A., 1916, ii, 636, 637).—It has already been emphasised that the rate at which hydrogen is absorbed in the "chlorate pipette" (sodium chlorate solution activated by osmium tetroxide; porous rods impregnated with platinum and a little palladium) is greatly lessened by traces of carbon monoxide. In order to render this influence most obvious, it is not advisable to consider the observed rate of absorption, for this depends on the surface area of the platinised tubes which reach out into the gas, and these become more and more immersed in the chlorate solution as the oxidation proceeds. The exposed surface is obviously proportional to the volume of gas left unabsorbed, for the tubes are arranged vertically in a cylindrical part of the apparatus, and therefore it is possible to arrive at the "relative rate of absorption." With pure hydrogen, this relative rate is constant, or slowly rises, until half the gas is absorbed, whilst traces of carbon monoxide cause a rapid fall in this rate. If the pipette is standardised and a curve is plotted connecting the relative rates of absorption at "half volume" with various proportions of carbon monoxide, the phenomenon can be employed further for quantitative purposes.

J. C. W.

**Estimation of Chlorine in Urine.** EMIL VOTOČEK (*Chem. Zeit.*, 1918, **42**, 317—318).—Ten c.c. of the urine are diluted with water to about 160 c.c., 5 c.c. of nitric acid and 6 drops of sodium nitroprusside solution (0·6 gram of the salt in 3 c.c. of water) are added, and the mixture is titrated with *N*/10-mercuric nitrate solution until a turbidity develops; the turbidity, when the end-point is reached, should not disappear within less than two minutes.

W. P. S.

**Detection and Estimation of Bromine, especially in Mineral Waters.** JOSÉ CASARES and A. TASTET (*Anal. Fis. Quim.*, 1918, **16**, 226—228).—A modification of Guareschi's method of estimating bromine (A., 1912, ii, 1208) which enables 0·0002 gram of bromine per litre to be detected.

A. J. W.

**Volumetric Estimation of Sulphur in Pyrites and Slag.** ERNEST MARTIN (*Mon. Sci.*, 1918, [v], **8**, ii, 149—150).—The slag or pyrites is treated with aqua regia, the solution evaporated to dryness, and the residue redissolved in dilute hydrochloric acid. The solution is diluted, and sodium carbonate added. The assay may also be opened out by fusion with sodium peroxide or a mixture of sodium carbonate and potassium nitrate, dissolved in water, and carbon dioxide passed through to precipitate lead. After filtration, methyl-orange is added, and the solution exactly neutralised with hydrochloric acid. The carbon dioxide is boiled off, and to the luke-warm solution a known volume of standard barium hydroxide and phenolphthalein are added. Carbon dioxide is bubbled through until the colour just changes, when the solution is cooled and titrated with *N*/2-hydrochloric acid.

F. C. T.

**Estimation of Thiosulphuric, Sulphurous, Trithionic, and Sulphuric Acids in a Mixture.** O. BILLETER and B. WAVRE (*Helvetica Chim. Acta*, 1918, **1**, 174—180).—The authors describe methods by which the above-named acids may be estimated in a mixture of all four. The total sulphur present is oxidised to sulphuric acid by warming with bromine water and the whole estimated as barium sulphate. The sum of the sulphite and thiosulphate is next estimated by titration with a standard iodine solution. The sulphite is then estimated alone by titration with a solution of sodium disulphide, according to the equation $Na_2S_2 + Na_2SO_3 = Na_2S + Na_2S_2O_3$.

The estimation is carried out in the presence of ammonium chloride at the boiling point, the end of the reaction being indicated by the persistence of the yellow colour of the standard solution. It is also advisable to circulate a current of carbon dioxide over the solution during titration.

Sodium trithionate reacts with sodium sulphide according to the equation $Na_2S + Na_2S_3O_6 = 2Na_2S_2O_3$, and consequently can then be estimated by a further titration with standard iodine. The reaction is carried out by boiling the solution with sodium sulphide for a few minutes, then adding sodium acetate and acetic acid and boiling to decompose excess of sulphide, and finally titrating with iodine. Should sulphite also be present, the thiosulphate titrated here will be made up (1) of that produced from the sulphite and (2) that produced from the trithionate, but as the amount due to the sulphite estimation is known, the calculation of the concentration of the trithionate follows. The method is very good, and in the estimation of the sulphite the end-point is emphasised by the appearance of a turbidity due to the liberation of sulphur. The amount of trithionate may be estimated by two other methods. (1) After the sulphite and thiosulphate have been titrated with iodine, sodium iodide is added and an excess of iodine, and the mixture heated under pressure; this oxidises the trithionate to sulphate. The same action occurs with the tetrathionate formed in the first estimation, and allowance must be made for this. After boiling for a few minutes, the flask is cooled and the excess iodine titrated with thiosulphate. (2) This method is based on the decomposition by trithionic acid according to the equation $H_2S_3O_6 = H_2SO_4 + SO_2 + S$. The mixture is acidified, and boiled while a current of carbon dioxide is passed through until all the sulphur dioxide has been expelled; the free sulphur is then filtered off and the sulphate estimated with barium chloride. This sulphate will represent 97·9—97·5% of the trithionate, and, of course, contains the sulphate originally present. J. F. S.

**[Analysis of Organo-selenium Compounds.]** FRITZ VON KONEK and OSKAR SCHLEIFER (*Ber.*, 1918, **51**, 852—855).—See this vol., i, 407.

**Micro-Dumas Estimation of Nitrogen in Liquids Poor in Nitrogen.** GEORG KRAEMER (*J. pr. Chem.*, 1918, [ii], **97**, 59—60).—The micro-Kjeldahl method for estimating nitrogen in small quantities of liquids such as milk can be replaced satisfactorily by a micro-Dumas process working with approximately 0·25 c.c. [See also *J. Soc. Chem. Ind.*, 526A.] D. F. T.

**The Estimation of Nitrogen by the Kjeldahl Method.** A. VILLIERS and (MLLE.) A. MOREAU-TALON (*Bull. Soc. chim.*, 1918, [iv], **23**, 308—311).—The authors advocate the combination of the method in which potassium sulphate is used with that in which mercury is used. The substance is digested with potassium sulphate and sulphuric acid until colourless, and, after partial cooling, 1 gram of mercury is added, and the digestion is continued for a quarter of an hour after the mixture has boiled. The remainder of the estimation is carried out as usual. W. G.

**The Estimation of Ammonia and Hydrochloric Acid by Weighing as Ammonium Chloride.** A. VILLIERS (*Bull. Soc. chim.*, 1918, [iv], **23**, 306—308).—The author reaffirms the accuracy of his method (compare A., 1900, ii, 310) for the estimation of ammonia or hydrochloric acid by weighing as ammonium chloride. W. G.

**Estimation of Ammonia in Urine, Serum, etc.** H. WIESSMANN (*Landw. Versuchs.-Stat.*, 1918, **91**, 346—352).—Distillation in the presence of dilute sodium carbonate solution at 50° and under 5 to 10 mm. pressure is recommended; urea does not yield any ammonia under these conditions. [See, further, *J. Soc. Chem. Ind.*, 532A.] W. P. S.

**Estimation of Nitrates and Nitrites.** WILHELM STRECKER (*Ber.*, 1918, **51**, 997—1004).—Two well-known reactions are employed for the estimation of nitrites and nitrates in mixtures, namely, those represented by the equations $NO_2' + NH_4^{\cdot} = N_2 + 2H_2O$ and $NO_3' + 3Fe^{\cdot\cdot} + 4H^{\cdot} = NO + 3Fe^{\cdot\cdot\cdot} + 2H_2O$. The solution to be analysed, containing nitrites and nitrates equivalent to not more than 0·11 gram $NaNO_2$ and 0·18 gram $KNO_3$, is dropped into a boiling, concentrated solution of ammonium chloride, at least 100 times as much of this salt being taken as the nitrite present, the solution being in a flask which is provided with an apparatus for producing air-free carbon dioxide on the one hand, and a water-cooled Schiff's nitrometer containing potassium hydroxide on the other. After adjusting the pressure and noting the volume of nitrogen, a solution of iron in concentrated hydrochloric acid is introduced and the nitric oxide collected.

The process and apparatus are minutely described, but contain no novel features. J. C. W.

**The Estimation of Phosphoric Acid as Magnesium Pyrophosphate. III. The Compound Magnesium Tetra-ammonium Diphosphate.** D. BALAREFF (*Zeitsch. anorg. Chem.*, 1918, **103**, 73—78. Compare this vol., ii, 266).—The presence in solution of a large quantity of ammonium chloride when magnesium ammonium phosphate is precipitated affects the purity of the precipitate and the accuracy of the result, which is low if the magnesium chloride is added to the phosphate solution, high if precipitation is carried out the reverse way. The presence of an excess of ammonium ions is likely to favour the formation of the compound $Mg[(NH_4)_2PO_4]_2$, but attempts to isolate this substance have failed. The precipitate of magnesium ammonium phosphate obtained from a solution saturated with ammonium chloride is found to be partly insoluble in hydrochloric acid after calcination, the insoluble portion being magnesium metaphosphate, and amounting to 10—17% of the weight of the calcined precipitate. Experiments show that the metaphosphate decomposes slowly when heated with a blast flame, more quickly, however, than the pyrophosphate.

The metaphosphate is probably not formed by the direct decomposition $Mg[(NH_4)_2PO_4]_2 = Mg(PO_3)_2 + 2NH_3 + 4H_2O$. There is always a certain loss of phosphoric acid, which can be accounted for by the decomposition of magnesium tetra-ammonium diphosphate according to the equation $Mg[(NH_4)_2PO_4]_2 = MgNH_4PO_4 + (NH_4)_3PO_4$. The ammonium phosphate dissociates on heating, part of the phosphoric acid being volatilised, part reacting with pyrophosphate to form metaphosphate. E. H. R.

**The Estimation of Phosphoric Acid as Ammonium Phosphomolybdate.** A. Villiers (*Bull. Soc. chim.* 1918, [iv], **23**, 305—306).—The author considers that his method (compare A., 1893, ii, 434), in which the phosphate is precipitated as ammonium phosphomolybdate and weighed as such under definite conditions, is more accurate than that of Clarens (compare this vol., ii, 128). W. G.

**A New Method of Qualitative Analysis without the Use of Hydrogen Sulphide.** Gustav Almkvist (*Zeitsch. anorg. Chem.*, 1918, **103**, 221—239).—The new method, which is described in detail, can be outlined as follows. The sample is first brought into solution, using aqua regia if necessary, but any residue insoluble in aqua regia need not be filtered off. Potassium hydroxide is added to the solution until its strength is about *N*, followed by potassium carbonate and hydrogen peroxide, the last to destroy oxalic acid and bring chromium into solution. The metals remaining in solution, forming Group I, are arsenic, antimony, tin, lead, zinc, aluminium, and chromium. All other commoner metals are precipitated, forming Group II, except sodium, potassium, and ammonium, which form Group III.

The solution containing Group I is divided into two parts. One part is reduced with iron and hydrochloric acid, whereby arsenic and antimony are reduced to metal, and eventually to their hydrides, which are identified by distillation, tin to stannous chloride. The second part of the solution is treated with sodium sulphide solution in excess, lead and zinc being precipitated as sulphides, chromium as hydroxide, aluminium remaining in solution as aluminate. The aluminium is precipitated as carbonate by a stream of carbon dioxide, the other elements of the group being identified by usual tests.

The precipitate containing the elements of Group II is dissolved by treatment with nitric acid and hydrogen peroxide. The insoluble portion, including that part of the sample originally insoluble in aqua regia, is worked up by usual methods. The solution is treated with freshly precipitated stannic hydroxide and evaporated to dryness to precipitate silicic, phosphoric, arsenic, and antimonic acids, and again extracted with nitric acid. The acid solution is then made strongly alkaline and boiled with hydrogen peroxide to precipitate iron, bismuth, and manganese, then ammonium oxalate added to precipitate calcium, strontium, and barium. The combined precipitates are evaporated with acetic acid, when calcium, strontium, and barium dissolve as acetates, iron, bismuth, and manganese being undissolved. The individual elements are identified by usual tests.

The filtrate from the iron–barium precipitates contains silver, mercury, copper, cadmium, nickel, cobalt, and magnesium. Silver and mercury are precipitated as metal by means of hydrazine sulphate, copper as cuprous thiocyanate, and the remaining metals detected by special tests.

The method does not claim to effect complete separations of the different groups, but it is efficient for the qualitative detection of the common elements. The modifications of procedure necessary when acid radicles are present which may lead to the formation of complex metallic compounds are described in detail. E. H. R.

**Sulphide Precipitation of Group 2a Metals.** JOSEPH SHIBKO (*Chem. News*, 1918, **117**, 253—254).—When these metals are precipitated from a slightly acid solution of a brass or bronze by ammonium sulphide instead of hydrogen sulphide, the precipitate contains small quantities of zinc. [See also *J. Soc. Chem. Ind.*, 517A.] C. S.

**Petersen's Method for the Qualitative Separation of the Cations of the so-called Third and Fourth Groups.** IWAN BOLIN and GUNNAR STARCK (*Zeitsch. anorg. Chem.*, 1918, **103**, 69—72).—A number of modifications of Petersen's process (A., 1910, ii, 654) are suggested. After precipitating the metals of the second group with hydrogen sulphide, Petersen precipitates strontium and barium with sulphuric acid. Instead, the authors use sodium sulphate. The precipitate is washed with hot water and the washings are tested for calcium with ammonium oxalate. The residue is then ignited with a little pure carbon, dissolved in 4*N*-acetic acid and examined for barium and strontium in the usual way. The authors prefer reduction with carbon to fusion with sodium carbonate.

In the separation of chromium from a mixture of iron, manganese, chromium, calcium, and magnesium hydroxides, it is better to oxidise the chromium to chromate with sodium hypochlorite. When sodium peroxide is used, it cannot be completely washed from the residue, and on acidification the hydrogen peroxide formed reduces manganese dioxide, and the manganese, passing into solution with calcium and magnesium, is precipitated with the latter.

For detecting zinc in the group of metals precipitated by sodium sulphide, the precipitate is boiled with alkaline sodium hypochlorite, zinc and chromium passing into solution. The solution is acidified with acetic acid, the chromate precipitated with barium chloride, and the filtrate tested for zinc with ammonium sulphide.

In presence of oxalic acid, the test for aluminium always fails.

Oxalic acid, if present, should be destroyed by boiling with 3% hydrogen peroxide and sulphuric acid. The Petersen process, with these modifications, gives very satisfactory results. E. H. R.

**Estimation of Magnesia in Water.** M. MONHAUPT (*Chem. Zeit.*, 1918, **42**, 338).—The water is neutralised, using methyl-orange as indicator, treated with a quantity of potassium oxalate slightly in excess of the amount of calcium oxide in the water, and a definite excess of $N/10$-alkali solution (prepared by mixing equal volumes of $N/10$-sodium hydroxide and sodium carbonate solutions) is added; the solution is diluted to a definite volume, filtered, an aliquot portion of the filtrate treated with a quantity of calcium chloride equivalent to the oxalate added, and the excess of alkali then titrated with $N/10$-acid. W. P. S.

**Gravimetric and Volumetric Determination of Zinc Precipitated as Zinc Mercury Thiocyanate.** GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1918, **40**, 1036—1039).—Lundell and Bee's method of estimating zinc in alloys as zinc mercury thiocyanate (*Trans. Amer. Inst. Met.*, 1914, 146) is subjected to criticism, the more important being: (1) arsenious compounds need not be removed, and (2) the factor for obtaining the weight of zinc is 0·13115, not 0·1266, since the precipitate, after being dried at 102—108°, has the composition $ZnHg(SCN)_4$, not

$$ZnHg(SCN)_4,H_2O.$$

Instead of weighing the zinc mercury thiocyanate, a trustworthy volumetric method of estimating the zinc in it is described, based on the reaction $ZnHg(SCN)_4 + 6KIO_3 + 12HCl = ZnSO_4 + HgSO_4 + 2H_2SO_4 + 4HCN + 6ICl + 6KCl + 2H_2O$. C. S.

**A New Reaction of Osmium.** L. TSCHUGAEV (*Compt. rend.*, 1918, **167**, 235).—When a solution containing osmium in the form of its tetroxide or as an osmichloride is warmed for a few minutes with thiocarbamide in excess and a few drops of hydrochloric acid, the liquid becomes coloured a deep red or a rose colour, according to the concentration of the osmium. By this means, osmium may be detected at a dilution of 1 in 100,000. The red *compound* has the composition $[Os,6CS(NH_2)_2]Cl_3,H_2O$, and is thus analogous to the luteo-cobalt salts. W. G.

**New Method for the Rapid Destruction of Organic Matter.** PAUL DURET (*Compt. rend.*, 1918, **167**, 129—130).—The method consists in boiling the material with 10% sulphuric acid and ammonium persulphate until all brown coloration has disappeared, repeated additions of ammonium persulphate being made if necessary. The method is applicable to urines, hair, wool, and also to such substances as sugars, fats, glycerol, and cacodyl compounds. W. G.

**Pregl's Microanalytical Estimation of Methyl Groups attached to Nitrogen.** S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1918, **101**, 278—287).—An account of the difficulties encountered in carrying out Pregl's method, and of various improvements by means of which they have been overcome, the principal being the adoption of a quartz flask instead of one of glass and the addition of a catalyst, gold chloride, which so accelerates the cleavage of the alkyl groups that the whole operation can be completed in one distillation occupying about thirty minutes. H. W. B.

**Reaction of Guaiacol Carbonate. A Test for Ethyl Ether.** G. MAUE (*Pharm. Zeit.*, 1918, **63**, 255—256).—To identify the presence of guaiacol in guaiacol carbonate, 0·02 gram of the latter is dissolved in 1 c.c. of alcohol, 2 drops of ferric chloride solution and 1 drop of formaldehyde solution are added, and 2 c.c. of sulphuric acid are then run in so as to form a layer under the mixture. A cherry-red ring develops at the junction of the two liquids. The test may be used for the detection of aldehydes in ethyl ether; although aldehydes other than formaldehyde do enter into the reaction, the author has found that the aldehydes which may be present in ethyl ether always include some formaldehyde. One c.c. of the ether is mixed with 0·02 gram of guaiacol carbonate, 1 c.c. of water and 1 drop of ferric chloride solution, and 2 c.c. of sulphuric acid are added. Pure ethyl ether for anæsthetic uses should not yield a red-coloured zone (absence of aldehydes); ordinary ether usually gives a reaction with the test. The sensitiveness of the test is 1 in 300,000. W. P. S.

**Estimation of Cholesterol in Blood Serum.** ADOLPH BERNHARD (*J. Biol. Chem.*, 1918, **35**, 15—18. Compare Weston, A., 1917, ii, 156).—The new method combines the extraction method of Weston and Kent and the colorimetric method of Grigaut (*Compt. rend. Soc. Biol.*, 1910, **68**, 827). The cholesterol is extracted by a mixture of alcohol and ether (1 : 1), and an estimation can be completed in five hours. H. W. B.

**Cleavage of Digitonincholesteride.** A. WINDAUS (*Zeitsch. physiol. Chem.*, 1918, **101**, 276—277. Compare Lifschütz, this vol., ii, 179).—The author gives further details of his method for the preparation of cholesteryl acetate from digitonincholesteride, but points out that the cleavage is more readily accomplished by the action of hot xylene (Windaus, A., 1910, ii, 462) or by one of the more recent methods, involving the use of acetic anhydride (see Prescher, A., 1917, ii, 275). H. W. B.

**Rate of Production of Colour in Alkaline Solutions of Dextrose and Picrate.** T. ADDIS and A. E. SHEVKY (*J. Biol. Chem.*, 1918, **35**, 43—51. Compare this vol., ii, 247).—A full account of work previously published. H. W. B.

**Modification of the Picrate Method for the Estimation of Dextrose in Blood.** T. Addis and A. E. Shevky (*J. Biol. Chem.*, 1918, **35**, 53—59).—The chief modification consists of the utilisation of a graph showing the increase of intensity of colour corresponding with increase in the concentration of dextrose for correcting the values for the dextrose in blood obtained by the picrate method of estimation. H. W. B.

**Estimation of Dextrose by [Sodium] Hypoiodite.** Richard Willstätter and Gustav Schudel (*Ber.*, 1918, **51**, 780—781).—The dextrose solution is mixed with about twice the amount of 0·1*N*-iodine solution necessary for oxidation to gluconic acid, a quantity of 0·1*N*-sodium hydroxide which is 1·5 times as much as the iodine is slowly added, the mixture is left for twelve to fifteen minutes (or twenty minutes if the proportion of sugar is very small), and then the excess of iodine is titrated after slightly acidifying with sulphuric acid. Taking 10 c.c. of sugar solution, the average error is less than 0·1% with 1% solutions, or less than 1·5% with 0·1% solutions.

Under these conditions, ketoses and sucrose are not affected, and therefore the method will be very useful in the estimation of aldoses in mixtures. The fundamental reaction is expressed thus:

$$OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot CHO + I_2 + 3NaOH = OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot CO_2Na + 2NaI + 2H_2O.$$

J. C. W.

**Detection of Sugar in Urine by means of an Alkaline Copper Solution.** H. Ruoss (*Zeitsch. physiol. Chem.*, 1918, **101**, 193—209).—A modification of the Worm-Müller test is described in which the quantity of the alkaline copper reagent to be boiled with 5 c.c. of the urine depends on the density of the urine. The number of c.c. of reagent required is determined by the formula $83(D-1)+0·7$, where $D$ is the density of the urine. If a deposit of red cuprous oxide fails to form when the calculated volume of the reagent is mixed with 5 c.c. of urine under the prescribed conditions of temperature and dilution, the urine is normal. By the addition of glycerol to the reagent, its delicacy is greatly increased, so that the presence of dextrose may be detected in even normal urines. H. W. B.

**Estimation of Lactose in Admixture with Sucrose and Invert-sugar.** J. Grossfeld (*Zeitsch. Nahr. Genussm.*, 1918, **35**, 249—256).—The following formulæ, deduced from the results obtained by experiments with the pure sugars, are given for calculating the quantity of lactose in a mixture also containing sucrose and invert-sugar. The mixed sugars are inverted by heating 50 c.c. of their solution at 100° for thirty minutes with 2 c.c. of hydrochloric acid (D 1·125), and the optical rotation and reducing power of the solution are then determined, the rotation being observed after the solution has remained for twenty-four hours.

Lactose $= 0·01375Z(D + 16·7)$ and sucrose $= 0·01145Z(79·6 - D)$, where $Z$ is the total reducing sugar (as invert-sugar) and $D$ its specific rotation. W. P. S.

**Detection of Methylpentosans.** KINTARO ŌSHIMA and KINSUKE KONDŌ (*J. Tokyo Chem. Soc.*, 1918, **39**, 185—198).—Methylpentosans frequently occur together with pentosans in vegetable substances. In such a case, Ōshima and Tollens's method (A., 1901, ii, 484) for detecting methylpentosans is the most sensitive. If other hydrocarbons of the hexose group are present in addition to methylpentosans and pentosans, the spectroscopic determination of methylfurfuraldehyde in Ōshima and Tollens's method needs some skill, as hydroxymethylfurfuraldehyde derived from hexose will also be found, and its absorption spectrum closely resembles that of methylfurfuraldehyde. The authors describe an improved method depending on the fact that hydroxymethylfurfuraldehyde can be destroyed completely by distillation with hydrochloric acid. Three to five grams of the sample are distilled according to Kröber and Tollens's method (compare A., 1902, ii, 288, 537). When the volume of the distillate reaches 300 c.c., 100 c.c. of it are taken and subjected to a second distillation. When 30 c.c. of liquid have distilled, an equal amount of the first distillate is run into the distilling flask by means of a separating funnel. This procedure is repeated until the whole of the first distillate has been added; the distillation is then continued with additions of hydrochloric acid (D 1·06) in the same manner until the total volume of distillate amounts to 400 c.c. To 5 c.c. of the second distillate, an equal volume of concentrated hydrochloric acid is added, and then a small quantity of a solution of phloroglucinol in hydrochloric acid (D 1·06). After five minutes or more, the precipitate of phloroglucide is filtered off and the absorption band of methylfurfuraldehyde determined in the filtrate. S. H.

**Sudan III. and the Detection of Fat.** V. H. MOTTRAM (*Proc. Physiol. Soc.*, 1918, xviii—xix, *J. Physiol.*, **52**; from *Physiol. Abstr.*, 1918, **3**, 162—163).—For the detection of fat in physiological mixtures, 1 gram of the powdered solid is shaken with 10 c.c. of a saturated solution of Sudan III in 70% alcohol. The colour of the filtrate is compared with that of the control (1 gram of fat-free starch, etc., similarly treated). If the filtrate is markedly lighter in colour, more than 0·04% of fat is present. For the detection of fat in milk, the curd is treated with acetic acid and filtered; the contents of the filter are treated as above. S. B. S.

**Estimation of Anthraquinone.** HARRY F. LEWIS (*J. Ind. Eng. Chem.*, 1918, **10**, 425—426).—Anthraquinone mixed with large amounts of anthracene or phenanthraquinone may be estimated by boiling the mixture with an excess of 5% sodium hydroxide solution and zinc dust; the reduction product is soluble in alkaline solution, and is separated from the insoluble substance by filtration. Re-oxidation occurs when the filtrate is shaken with air, and the resulting anthraquinone is then collected, dried, and weighed. W. P. S.

**Analysis of Commercial "Saccharin." Estimation of *o*-Benzoylsulphonimide from the Ammonia Produced by Acid Hydrolysis.** H. Droop Richmond and Charles Alfred Hill (*J. Soc. Chem. Ind.*, 1918, **37**, 246—249T).—The various methods available for the analysis of "saccharin" are criticised. It is shown that Reid's hydrochloric acid method (A., 1899, ii, 581) is accurate but rather troublesome. Proctor's method (T., 1905, **87**, 242) tends to low results; it is insufficiently described and leads to discrepancies between analyses. By increasing the time of hydrolysis to four hours or the strength of the acid to 1·5*N*, it becomes trustworthy. The following method is recommended. The "saccharin" is boiled for two minutes with 10 c.c. of 7·5*N*-sodium hydroxide to expel free ammonia, and then for fifty minutes with 15 c.c. of 10*N*-hydrochloric acid, using an efficient reflux condenser. The liquid is cooled and 75 c.c. of cold water are added; 15 c.c. of 7·5*N*-sodium hydroxide are added, and the ammonia is distilled into 20 c.c. of 0·2*N*-hydrochloric acid. The excess of acid is then titrated with 0·1*N*-alkali, using methyl-red as indicator. J. F. S.

**Identification of the Cinchona Alkaloids by Optical-crystallographic Measurements.** Edgar T. Wherry and Elias Yanovsky (*J. Amer. Chem. Soc.*, 1918, **40**, 1063—1074).—Cinchonine, cinchonidine, quinine, and quinidine are separately crystallised from alcohol or benzene, and the crystals are optically examined under the microscope in ordinary light and in parallel and in convergent polarised light; the refractive indices are measured by the immersion method in solutions of potassium mercuric iodide and glycerol of known indices. Tables of the data thus obtained are given. It is shown that the individual alkaloids in a mixture of the four can be identified by the data, and a description is given of the application of the method to the identification of the alkaloids in a medicinal preparation. [See *J. Soc. Chem. Ind.*, 529A.] C. S.

**Colorimetric Estimation of Brucine in Presence of Strychnine.** A. Wöber (*Zeitsch. angew. Chem.*, 1918, **31**, i, 124).—The drawback of Dowzard's colorimetric method of estimating brucine in presence of strychnine (P., 1902, **18**, 220) is that the coloration fades with varying velocity according to the concentration of the alkaloid solution. The strong nitric acid used for the reaction also affects the strychnine, producing a yellow coloration. The method may be rendered trustworthy by using a mixture of equal volumes of strong nitric acid (D 1·4) and 20% sulphuric acid as the reagent, and adding a small amount of a saturated aqueous solution of potassium chlorate immediately after the reaction. The standard brucine solution used for the comparison should contain 0·1 gram of strychnine. [See also *J. Soc. Chem. Ind.*, 441A.] C. A. M.

**Extraction of Nicotine from Aqueous Solutions.** KARL DANGELMAJER (*Chem. Zeit.*, 1918, **42**, 290).—Trichloroethylene is a useful solvent for extracting nicotine from its alkaline aqueous solution; the extraction is quantitative, and the nicotine may be recovered from the trichloroethylene solution by shaking the latter with dilute sulphuric acid. W. P. S.

**Identification of Novocaine.** J. A. SANCHEZ (*Rev. farm. Buenos-Ayres*, 1917, 699; from *Ann. Chim. anal.*, 1918, **23**, 137). —A red coloration is obtained when a 0·2% novocaine solution is heated with 2 drops of 10% sodium nitrite solution and 3 drops of sulphuric acid, then diluted with water and treated with Millon's reagent. This reaction identifies the phenolic nucleus of the substance. The ethylic nucleus is identified by the formation of iodoform, and the aldehydic nucleus by distilling the substance with dilute sulphuric acid and manganese dioxide and testing the filtrate with magenta-sulphurous acid reagent. With bromine, novocaine yields a yellow precipitate, which dissolves when the mixture is heated. W. P. S.

**The Colorimetric Estimation of Hæmoglobin as Acid Hæmatin.** LADISLAUS BERCZELLER (*Biochem. Zeitsch.*, 1918, **87**, 23—35).—By means of an Autenrieth colorimeter, hæmoglobin can be estimated as acid hæmatin, when a washed suspension of corpuscles is employed. The method cannot, however, be employed for determining the amount of hæmolysis in, for example, the Wassermann reaction, as it is interfered with both by the presence of serum and the solution of the antigen in organic solvents. S. B. S.

**Tryptoproteases.** M. FRANCESCO (*Arch. farm. sper. sci. aff.*, 1917, **24**, 3—22; from *Physiol. Abstr.*, 1918, **3**, 165).—From a comparative study of nine methods for determining the presence of trypsin, the author recommends the gelatin method of Fermi as the most delicate and trustworthy. It is fifty times as sensitive as the serum and casein methods for the protease of some of the pathogenic bacteria. S. B. S.

# General and Physical Chemistry.

**Comparative Study of the Flame and Furnace Spectra of Iron.** G. A. HEMSALECH (*Phil. Mag.*, 1918, [vi], **36**, 209—230).—A direct comparison has been made of the flame and furnace spectra of iron by the use of the same dispersion apparatus in the two series of observations. In the production of the furnace spectrum, finely divided oxide of iron was introduced into an electrically heated carbon tube by means of a current of air which had previously passed through a glass bulb enclosing an arc burning between iron electrodes.

The furnace spectrum makes its appearance at about 1500°, and at this temperature the spectrum is the same as that obtained with an air flame burning in coal gas. Up to about 2400°, the flame spectra are identical with those given by the furnace at corresponding temperatures. This identity suggests that the cause of the emission is the same under the different conditions obtaining in the two series of observations, and the author supposes that the spectrum is directly due to the thermochemical dissociation of iron compounds. Above 2500°, the furnace spectrum undergoes a radical change, and it is supposed that this is due to the electrical conduction of the vapour.

In contrast with the above parallelism between flame and furnace spectra, it is noteworthy that the iron spectrum emitted by iron in the inner cone of an air–coal gas flame, the temperature of which is less than 1700°, contains lines which are entirely absent from the flame or furnace spectrum up to 2500°. Some of these lines are shown very feebly by an oxy-acetylene flame at a temperature of about 2700°, but their intensity is very much less than that of the lines in the explosive region of the air–coal gas flame. This anomaly in the behaviour of the low temperature Bunsen cone is attributed to the affinity of iron for nitrogen, with the formation of a nitride. The cause of the emission is accordingly chemical, and the chemical excitation at a comparatively low temperature is equivalent to that produced by thermochemical excitation at a very much higher temperature. In its development, the cone emission approaches, in fact, that of the self-induction spark.

H. M. D.

**Spectrochemical Notes. I. Polyketo-compounds. II. Allene and Keten. III. Spectrochemical Practice.** K. VON AUWERS (*Ber.*, 1918, **51**, 1116—1133).—I. This section discusses the influence of the introduction of conjugated carbonyl groups in a compound on the refraction and dispersion. As the subjoined table shows, the simple conjugation –CO·CO– causes unimportant exaltations, which are not much more marked when further carbonyl groups are introduced, but conjugations with an ethylene linking of the types $-C:C\cdot C:O$, and especially $-C:C-CO\cdot CO-$, cause very considerable exaltations in refraction and dispersion.

| Formula. | $E\Sigma_{\alpha}$. | $E\Sigma_{D}$. | $E\Sigma_{\beta}-\Sigma_{\alpha}$. | $E\Sigma_{\gamma}-\Sigma_{\alpha}$. |
|---|---|---|---|---|
| $CH_3\cdot CO\cdot COMe$ | +0·42 | +0·41 | +9% | — |
| $CO_2Et\cdot CO_2Et$ | 0·27 | 0·27 | 4% | 4% |
| $CH_3\cdot CO\cdot CO\cdot CO_2Et$ | 0·60 | 0·60 | — | — |
| $CO(CO_2Et)_2$ | 0·57 | 0·56 | 10% | — |
| $C_2O_2(CO_2Et)_2$ | 0·68 | 0·68 | — | — |
| $C_6H_5\cdot CO\cdot COMe$ | 1·01 | 1·05 | — | — |
| $COPh\cdot CO\cdot COMe$ | 1·37 | 1·45 | — | — |
| ($p$)$OMe\cdot C_6H_3Me\cdot CO\cdot COMe$ | 1·27 | 1·35 | 80% | — |
| ($p$)$OEt\cdot C_6H_3Me\cdot CO\cdot COMe$ | 1·46 | 1·53 | 78% | — |
| $C_6H_5\cdot CO\cdot CO_2Et$ | 0·89 | 0·94 | 46% | 52% |

Most of the above compounds are already well known, but complete physical data are recorded in each case, for which the original should be consulted. p-*Ethoxy*-o-*tolyl methyl diketone*, $OEt\cdot C_6H_3Me\cdot CO\cdot COMe$, appears to be new. It crystallises in glassy prisms, m. p. 63—64°, has $D_4^{65}$ 1·0524, $n_{\alpha}$ 1·50733, $n_D$ 1·51270, $n_{\beta}$ 1·52888, at 65°, and is prepared as follows. *o*-Propionyl-*p*-cresol is ethylated by means of ethyl sulphate, the p-*ethoxy*-o-*tolyl ethyl ketone*, m. p. 50—51°, is treated with amyl nitrite and hydrochloric acid, and the *oxime*, m. p. 105—106°, is hydrolysed by boiling sulphuric acid.

II. In this chapter, it is shown that compounds with cumulated ethylene linkings exhibit considerable exaltations in refraction and dispersion. For example, *αα*-dimethylallene, $CMe_2:C:CH_2$, b. p. 39—40·5°, has $E\Sigma_{\alpha}$ +0·60, $E\Sigma_{D}$ 0·59, $E\Sigma_{\beta}-\Sigma_{\alpha}$ + 21%, $E\Sigma_{\gamma}-\Sigma_{\alpha}$ 18%. This is contrary to Brühl's rule (*Ber.*, 1907, **40**, 1160), but is supported by the results obtained by Mereschkowski with *s*-tetramethylallene and *αα*-diethylallene (A., 1914, i, 369). The influence of adjacent pairs of ethylene linkings is by no means so great as that of conjugated double bonds, however; piperylene, $CHMe:CH\cdot CH:CH_2$, for example, has $E\Sigma_{\alpha}+1{\cdot}81$, $E\Sigma_{D}$ 2·10, $E\Sigma_{\gamma}-\Sigma_{\alpha}+53\%$.

Ketens have a similar system of cumulated double bonds, $-C:C:O$, but this system has no special optical influence, as the following table shows:

| Formula. | $E\Sigma_{\alpha}$. | $E\Sigma_{D}$. | $E\Sigma_{\beta}-\Sigma_{\alpha}$. |
|---|---|---|---|
| $Ph_2C:O$ | +0·91 | +1·00 | — |
| $Ph_2C:CH_2$ | 0·88 | 0·95 | — |
| $Ph_2C:C:O$ | 0·86 | 0·92 | — |
| $Et_2C:C:O$ | −0·08 | −0·09 | −2% |

The polymeride of diethylketen, namely, 1:1:3:3-tetraethyl*cyclo*butan-2:4-dione, has $E\Sigma_{\alpha}+0{\cdot}27$, $E\Sigma_{D}+0{\cdot}25$, $E\Sigma_{\beta}-\Sigma_{\alpha}$ +4%, $E\Sigma_{\gamma}-\Sigma_{\alpha}$ +1%, the increments being of the order normally associated with the four-membered ring system.

III. For the determination of the density of molten substances, the author recommends an ordinary pyknometer with a portion of one of its capillaries, about 2 cm. long, graduated in millimetres. Such an instrument is calibrated for different points along this scale, and in an actual determination the position of the liquid in the tube is noted. J. C. W.

**Effects of Ring Closure on Spectrochemical Properties. I. Saturated Iso- and Hetero-cyclic Compounds, Unsaturated Isocyclic Substances, and the Question of the Constitution of Benzene.** K. von Auwers (*Annalen*, 1918, **415**, 98—168).—The author surveys a large field of material, and arrives at the following generalisations. Compounds the molecules of which contain one or more rings (isocyclic or heterocyclic) without linkings of any kind are optically normal; only when the ring is under tension do the molecular refraction and dispersion exhibit exaltation or depression. The spectrochemical character is unchanged when a saturated side-chain closes to form a ring; for example, the pairs *o*-tolyl methyl ether and coumaran and *o*-tolyl ethyl ether and chroman are optically identical, and the same holds for a large number of other coumarans and phenolic ethers. The closure of an unsaturated side-chain to a ring causes a weakening of the optical properties, which is the more pronounced the more unsaturated is the chain; for example, styrene derivatives and indene derivatives, acyclic dienes and cyclic dienes, and acyclic trienes and cyclic trienes. Alkyl groups and other substituents produce an effect opposed to that of ring closure in unsaturated compounds. Exceptions occur to all these generalisations.

Contrary to earlier views, double linkings in open and in closed chains are not optically equivalent, the spectrochemical effect of cyclic double linkings being quite generally slighter than that of ethylenic linkings.

The two physico-chemical methods of investigation, spectrochemistry and thermochemistry, both decide against the view that benzene and its hydrogenated derivatives are different in their innermost structure, and all the physical and chemical facts ally themselves best to a benzene formula containing three double linkings.

The densities and refractive indices of a number of compounds have been redetermined, and new determinations have been made in the case of a large number of coumarans, chromans, phenolic ethers, ketones, and indene derivatives.

The following substances are new: as.-m-*xylyl ethyl ether*, b. p. 202—203°, $D_4^{13\cdot95}$ 0·9487, $n_\sigma$ 1·50297, $n_D$ 1·50692, $n_\beta$ 1·51874, $n_\gamma$ 1·52872 at 13·95°; 5-*bromo*-o-*tolyl ethyl ether*, b. p. 238—240°, $D_4^{11\cdot35}$ 1·3592, $n_\alpha$ 1·54387, $n_D$ 1·54858, $n_\beta$ 1·56186, $n_\gamma$ 1·57332; 6-*ethoxy*-m-*toluic acid*, needles, m. p. 200—201°, and its *ethyl* ester, b. p. 274—275°, $D_4^{15\cdot1}$ 1·0618, $n_\alpha$ 1·51443, $n_D$ 1·51908, $n_\beta$ 1·53259, $n_\gamma$ 1·54428 at 15·1°; and 1-*methyl*-ac-*tetrahydro*-α-*naphthol*, colourless leaflets, m. p. 88—89°. C. S.

**Quinone-imide Dyes. X. Absorption Spectra of the Simplest Triphenylmethane Dyes.** F. KEHRMANN and M. SANDOZ (*Ber.*, 1918, **51**, 915—922. Compare this vol., i, 311).—Tables are given which record the shades of colour and absorption spectra of the various series of salts of triphenylcarbinol, its mono-, di-, and tri-amino-, and mono-, di-, and tri-dimethylamino-derivatives, the substituents being in the para-positions. It is shown that the highest salts in all cases, ranging from the di-acid salt of triphenylcarbinol to the tetra-acid salts of magenta and crystal-violet, and obtained by dissolving the dyes in concentrated sulphuric acid, give pure yellow solutions with practically the same absorption band, beginning at about $\lambda$ 480—490 $\mu\mu$. J. C. W.

**Quinone-imide Dyes. XI. Absorption Spectra of some Amino-derivatives of Naphthaphenazoxonium.** F. KEHRMANN and M. SANDOZ (*Ber.*, 1918, **51**, 923—928).—The absorption spectra of some amino-derivatives of 7:12-naphthaphenoxazine and their salts are recorded by tables of curves. The 5-amine is lemon-yellow and gives orange-yellow mono-acid salts and dark blood-red di-acid salts, all having the para-quinonoid configuration. The 9-amine is orange-yellow and gives magenta-coloured mono-acid, greenish-blue di-acid, and bluish-violet tri-acid salts. The 5:9-diamine is orange-coloured, and its salts are as follow: mono-, violet-blue with red fluorescence; di-, orange-yellow; tri-, dark blood-red. The 9-dimethylamino-derivative forms violet mono-acid and green di-acid salts. J. C. W.

**Action of Light on Crystals.** FRITZ WEIGERT (*Zeitsch. Elektrochem.*, 1918, **24**, 222—237).—The extinction of crystals and the phototropic changes occasioned by light of short wave-length have been examined in the case of $\beta$-tetrachloro-$\alpha$-ketonaphthalene. It is shown that no changes, other than the characteristic colour changes, are brought about in the crystallographic properties of $\beta$-tetrachloro-$\alpha$-ketonaphthalene by the action of light of short wave-length. The axial ratio remains constant even under strong illumination. The absorption spectrum of the crystals varies very much with the electric vector of the entering plane polarised light. When the crystal is not excited, two absorption bands, 395 $\mu\mu$ and 375 $\mu\mu$, are observed if the entering ray is vibrating in the direction of the *c*-axis, but if the entering ray is vibrating in the *a*-*b*-plane, an end absorption at 420 $\mu\mu$ is observed. With excited crystals and the entering light in the *c*-direction, there is no change in the absorption spectrum, whilst in the *a*-*b*-plane the absorption is much greater, and an absorption band appears in the yellow-green; this is due to the phototropic colouring. The absorption spectrum of the solutions of $\beta$-tetrachloro-$\alpha$-ketonaphthalene in ether and benzene shows no characteristic bands, but in the long wave-length ultra-violet two obvious steps appear in the same positions as the bands observed with the crystals. Hence it appears that the solid and dissolved molecules are identical. The effect for an equal quantity of energy when the electric vector is in the *c*-direction is greater than when it is in the *a*-*b*-plane, since the absorption is greater in the first case than in the second. The lighting up of the crystal by plane polarised yellow light only occurs when the electric vector vibrates in the *a*-*b*-plane. The maximum excitation of β-tetrachloro-α-ketonaphthalene will therefore only occur when plane polarised light swinging in the *c*-direction is allowed to fall on it, since in this case the light produces no brightening in the opposite direction. The fact that the coloration does not occur in the solution, but only in the crystal, shows that the ordered, closely packed orientation of the molecules in the crystal is the cause of the effect. The two possible formulæ for β-tetrachloro-α-ketonaphthalene are considered in the light of the present results, and it is shown that one only is in accord with them, namely, that with $Cl_2$ in the α-position. J. F. S.

**Temperature-coefficients of the Action of Light on the Chlorine-Hydrogen Mixture with Monochromatic Light.** M. Padoa and C. Butironi (*Gazzetta*, 1917, **47**, ii, 6—9).—The velocities of the combination of hydrogen and chlorine at 10°, 20°, 30°, and 40°, and for lights of different wave-lengths, have been measured, the mean temperature-coefficients being as follows: white light, 1·29; green ($\lambda=550$—530), 1·50; blue ($\lambda=490$—470), 1·31; violet ($\lambda=460$—440), 1·21; ultra-violet ($\lambda=400$—350), 1·17. T. H. P.

**History of Substances Sensitive to Light.** Boruttau (*Zeitsch. angew. Chem.*, 1918, **31**, 139—140).—The discovery of the colour change of silver salts under the influence of light is stated to be mentioned first by Konrad Gessner in 1565 in his work, "De omni verum fossilium genere libri aliquot," and not by Fabricius, as erroneously supposed. Gessner describes the darkening of natural hornsilver when exposed to light. The later history of the subject is traversed. H. J. H.

**The Parent-substance of Actinium, a New Radioactive Element of long Life-period.** Otto Hahn and Lise Meitner (*Physikal. Zeitsch.*, 1918, **19**, 208—218. Compare Soddy, Cranston, and Hitchins, this vol., ii, 211).—The history of the long search for the parent of actinium is detailed. The value for the half-period of actinium itself, given provisionally by Mme. Curie as of the order of thirty years, has been confirmed for an actinium preparation studied during seven years, as well as for several more recently prepared specimens. Early attempts to detect the parent of actinium in uranium salts led to no result. In the first successful experiment, 21 grams of powdered pitchblende were treated with hot concentrated nitric acid. Part of the undissolved siliceous residue, mixed with some mg. of potassium tantalum fluoride, was treated with hydrofluoric acid, which dissolved it for the most part, and the solution, after filtration and evaporation, was evaporated with concentrated sulphuric acid. Concentrated nitric acid dissolved most of the residue. The undissolved part was mounted on an aluminium sheet (Prep. I), and was found to give α-rays, which remained constant for some weeks and then slowly increased when the preparation was tested bare. Tested so as to cut out the α-rays of low range, the growth of the radiation was much more marked, increasing some sixfold in the course of a year, the growth being linear with the time after the first few weeks. This indicated that the siliceous residues from pitchblende contained the sought-for parent of the actinium, resembling tantalum in chemical character and giving α-rays of low range in producing actinium, the products of which give α-rays of long range.

This view was completely confirmed by working with larger quantities of rich pitchblende residues obtained from the Chininfabrik, Brunswick. These residues, after a preliminary treatment with hydrochloric acid in presence of a few mg. of tantalic acid, and after the addition of a few mg. of thorium nitrate, were treated as detailed for Prep. I. The rapid growth of the more penetrating α-radiation was confirmed, and the growth of an active deposit also found. After three weeks, no active deposit could be detected, but after five months an easily measurable quantity was found, and its growth thereafter could be followed and the active deposit itself shown to be that of actinium. The growth of the actinium emanation with time was also observed. For the measurement of the range of the α-rays and the quantitative study of the growth of emanation and active deposit, preparations were worked up by Giesel at the Chininfabrik from 1 kilogram of pitchblende residues by the method described. The weight was reduced to 16 grams, and from this 73 mg., mainly tantalic acid, was obtained as a white powder, one thousand times as active as the material from which it was separated, and weight for weight forty-six times as active as uranium oxide. Assuming that 8% of the uranium atoms disintegrating produce "protoactinium," the quantity in the 73 mg. is that in equilibrium with 86 grams of uranium.

Concordant measurements of the range of the α-rays gave 3·314 cm. in air at 0° and 760 mm. (wrongly given in the summary and elsewhere as 3·14 cm.). From the Geiger Nuttall relation, using the values for the constants *A* and *B* deduced from observations of the range of the α-rays of radio-actinium, the calculated half-life period is 180,000 years, but using the values found for the α-rays of actinium-*X*, the half-period calculated is 1200 years. It is of interest that in the latter research, Meyer, Hess, and Paneth observed for actinium itself a very feeble α-radiation of range 3·38 cm., which was probably due to admixed proto-actinium.

Using 45 mg. of the preparation, the growth of the actinium emanation was followed for 100 days, in which time the amount increased to thirty times that present at the first measurement four days from preparation. After the initial period of gradually increasing rate of growth, extending over forty days, due to the successive generation of radio-actinium and actinium-*X*, the growth continued linearly with the time. The growth of the active deposit from 9·5 mg. of the preparation was also followed. The active deposit showed a sevenfold increase between the first and the third month.

Protoactinium is one of the five new radio-elements occupying a place in the periodic table hitherto vacant, and the determination of its spectrum and atomic weight should be practicable. For each 1 gram of radium in uranium minerals there should be 60 mg. of protoactinium if its life is 1200 years and 9 grams if its life is 180,000 years. Its atomic weight is either 230 or 234, according as the actinium series is derived from uranium-*II* or uranium-*I*, and the former is indicated according to the Fajans generalisation, between atomic weight and life-period of isotopes, which makes the most probable value for the atomic weight of radioactinium 226. Its separation in quantity from pitchblende residue should enable purer preparations of actinium to be prepared than have yet been got, analogously to the preparation of radiothorium from old mesothorium preparations. It should prove to be a radioactive substance, the α-activity of which increases sixfold during the lapse of some generations and then remains constant and permanent.

F. S.

**The Life-period of Radiothorium, Mesothorium, and Thorium.** ʼLise Meitner (*Physikal. Zeitsch.*, 1918, **19**, 257—263).—Measurements extended over seven years of α-, β-, and also γ-rays of six preparations of radiothorium prepared by electrolytic and chemical methods all gave quite linear logarithmic decay curves, the half-period for the six preparations varying between 690 and 698 days, the mean being 696 days = 1·905 years, accurate to about 1%.

The life-period of mesothorium-*I* was determined by a new method from the growth of radiothorium from mesothorium initially quite free from radiothorium. Mesothorium as free as possible from radium was prepared from mantle-ash by the firm of Knöfler and Co., Plötzensee, the preparation being crystallised three times at fortnightly intervals to remove radiothorium and its products. Tested for radium, it was found that only 0·8% of the β-rays and 0·62% of the γ-rays were due to this element, which was corrected for. By comparing the curve obtained with theoretical curves drawn for various periods of mesothorium, the results were found to agree well with a value 6·7 years for the half-period. This new value was checked by observation of the decay of the activity of a preparation of mesothorium, prepared by Hahn in 1906 and 7·1 years old at the commencement of the measurements. The period again found, 6·7 years, is considerably higher than the value, 5·5 years, for the half-period of mesothorium commonly accepted. The maximum of the α-activity of a mesothorium preparation is calculated to be 4·83 years from preparation, and of the γ-rays, through 0·5 cm. of lead, 3·34 years. For preparations of equal α-activity of radium and radiothorium respectively in equilibrium with their

$\alpha$-ray products, the $\gamma$-rays of radium are 1·5 times those of radiothorium and 0·9 times those of radiothorium and mesothorium in equilibrium.

The life-period of thorium was calculated by a somewhat elaborate method depending on a comparison of the $\alpha$-rays of radium and thorium preparations under defined conditions, and found to be $2·37 \times 10^{10}$ years (period of half-change), which is somewhat greater than previous estimates—1·28 (Geiger and Rutherford), 1·86 (McCoy), 1·5($\times 10^{10}$ years) (Heiman). The above value is reduced to $2·16 \times 10^{10}$ years if the just published value for the half-period of radium is taken as 1580 years (Hess and Lawson). F. S.

**Radioactivity in Natural Sardinian Materials, with Minerogenetic Particulars.** Aurelio Serra (*Gazzetta*, 1917, **47**, ii, 1—5).—A Sardinian porphyritic granite is found to be radioactive, its activity being $\alpha = 0·00010$. The activity is shown to be due to the presence in the rock of uraniferous biotite; the biotite has been subjected to the action of water which has previously traversed strata of uraniferous mica, the thickness of the latter determining the greater or less radioactive power. T. H. P.

**Abnormality of Strong Electrolytes. II. Electrical Conductivity of Non-aqueous Solutions.** Jnanendra Chandra Ghosh (T., 1918, **113**, 627—638).—In a previous paper (compare this vol., ii, 215) it has been shown that the variation of the conductivity of aqueous solutions of salts with dilution can be satisfactorily accounted for by equations which the author has derived from certain assumptions relative to the nature of electrolytes. It is now shown that these equations may be applied with equal success to the conductivity of non-aqueous solutions of strong electrolytes. In all, some thirty different solvents have been examined with reference to the influence of dilution on the conductivity of one or more dissolved electrolytes.

The behaviour of Walden's "normal electrolyte" (tetraethylammonium iodide) can only be explained on the assumption that it at first undergoes polymerisation and then ionises as a ternary electrolyte in accordance with the equation $(NEt_4I)_2 = 2NEt_4{}^{\bullet} + I_2{}''$ or $(NEt_4I)_2 = (NEt_4)_2{}^{\bullet\bullet} + 2I'$.

From his observations on the conductivity of tetraethylammonium iodide in different solvents, Walden found that the product of the dielectric constant ($D$) and the cube root of the dilution ($V$), for which the degree of ionisation has a common value, is the same for all solvents. In other words, $D\sqrt[3]{V}$ is independent of the nature of the solvent. It is shown that this empirical relation follows at once from the author's equations, in which $\mu_v/\mu_\infty$ represents, however, the activity coefficient and not the degree of ionisation in the Arrhenius sense. H. M. D.

**Electromotive Behaviour of Oxygen and its Anodic Evolution below the Reversible Oxygen Potential.** G. Grube and B. Dulk (*Zeitsch. Elektrochem.*, 1918, **24**, 237—248).—With the object of ascertaining the nature of the process occurring on an anodically polarised platinum electrode during the evolution of oxygen, the authors have measured the oxygen potential on such an electrode which at the same time is polarised by a measured direct current and an alternating current. The latter acts in the same way as a depolariser of measured strength. Series of measurements are recorded for alternating currents up to 4·0 amperes and current densities up to 0·287 ampere per sq. cm. All measurements were made at 20° and in 2*N*-sulphuric acid. A further series of measurements is recorded for *N*-sodium hydroxide for depolarising currents up to 5·0 amperes and 0·358 ampere per sq cm. current density. It is shown that the depolarising action of the alternating current is due to the reduction of a platinum oxide by the cathodic component. If the alternating current is slowly increased in strength along with a steady direct current, the oxygen potential (that is, the anode potential) falls below the value for the reversible formation of oxygen. The potential curve obtained from the measurements falls into three parts which are separated by inflection points. The highest of these curves corresponds with $\epsilon_h = 2·0 - 1·5$ volts, the next to $\epsilon_h = 1·5 - 1·23$ volts, and the lowest with $\epsilon_h = 1·23 - 1·0$ volts. This compels the assumption that the electromotive activity of oxygen above its equilibrium potential causes the formation of two different platinum oxides. The oxide which is active over the region $\epsilon_h = 2·0 - 1·5$ volts is unknown and is higher than $PtO_3$. In the region $\epsilon_h = 1·5 - 1·23$ volts, the dissolved oxide $PtO_3$ brings about the evolution of oxygen, whilst below 1·23 volts the evolution of oxygen is due to the reaction $H_2O_2 + O \longrightarrow H_2O + O_2$. The hydrogen peroxide necessary for this change is produced by alternating current on the anode. The most probable value for the oxygen potential is given as $\epsilon_h = +1·23$ volts.

J. F. S.

**Kinetics of Reactions with Electrolytes in Homogeneous Systems.** RUD. WEGSCHEIDER (*Monatsh.*, 1918, **39**, 15—86).—A theoretical paper in which the kinetics of the various types of reactions with electrolytes are discussed. Replaceable electrolytes are characterised as those which have the same type of formulæ, are not ionised in stages, have the same dissociation constant, have either a common ion and only one unlike ion, or are binary electrolytes. In the case where all the electrolytes are replaceable, it is shown that they have the same degree of dissociation, and this depends on the total concentration of the electrolytes only. With electrolytes having dissimilar ions, the degree of dissociation does not depend on the electrolyte, but on the nature of the ion-forming radicles. If in a reaction only non-electrolytes and replaceable electrolytes are present, then the degree of dissociation does not change if the total concentration of the electrolytes does not change. In general, the course of an electrolytic reaction is different in accordance with whether a separation of electrolyte occurs or not. A statement is evolved which represents the change in dissociation of a non-replaceable electrolyte, in the presence of replaceable electrolytes, during the course of a reaction with constant total ion concentration. The relationship between the velocity constant, as obtained from the law of mass action, and the course of the reaction is examined for the case where only one electrolyte is active (1) as relating to the undissociated molecule, and (2) either as relating to all the ions or only to one ion of a given molecule. The case of simultaneous reactions with a single electrolyte, and reactions with two electrolytes are also considered. The regularities found in these cases are illustrated by means of well-investigated reactions. In the case of the barium catalysis of Abel and the cation catalysis of Holmberg, it is shown that the formulæ obtained are quantitatively accurate, despite the presence of strong electrolytes. It is clearly shown that the electrolytic dissociation theory is not only not disproved by chemical kinetics, but is strongly supported. Further, the view of the overwhelming importance of the ionic condition in bringing about chemical reactions must be very much restricted. It is also shown on what conditions the divergencies from the laws of chemical kinetics depend, and also how the sensitiveness of kinetic calculations depends on uncertainty of the value of the degree of dissociation. J. F. S.

**Electrochemical Behaviour of Molybdenum and some Molybdenum Compounds.** KUNO WOLF (*Diss. Tech. Hochschule Aachen*, 1918, 38 pp.; from *Chem. Zentr.*, 1918, i, 608—609).—For the electrolytic estimation of molybdenum, the metal is separated in the form of the hydrated sesquioxide, and is then dried and converted into the trioxide by ignition at 425°; sublimation occurs at 450°. The separated sesquioxide or hydroxide has an electrolytic and at first a pseudo-metallic conductivity. On account of the poor yield, the electrolytic preparation of hydrated molybdenum sesquioxide is not practicable. Pure molybdenum, freezing point 2250°, D 8·95, prepared from the commercial metal, can be formed into sticks without pressure, treatment with a current of hydrogen for five to six hours at 2250°, however, being necessary for the reduction of included oxides. Pure molybdenum free from oxide is converted by chlorine into black, deliquescent molybdenum pentachloride, which on treatment with hydrogen at 250° yields the deep brownish-red, amorphous trichloride; this, when heated in a current of carbon dioxide, decomposes gradually with formation of the volatile tetrachloride and the refractory pale yellow, amorphous dichloride; the lower chlorides of molybdenum are much more stable than the higher towards air and water. In the preparation of the dichloride from molybdenum, it is important to exclude every trace of oxygen, because when heated in air the dichloride gives a cloudy white sublimate and a black residue of oxide. The dichloride gives yellow solutions in aqueous sodium hydroxide or potassium hydroxide, which deposit the black dihydroxide when boiled. The alcoholic solution conducts the electric current, the molecular conductivity increasing on dilution; hydrogen and the oxychloride, $Mo_3(OH)_2Cl_4$, and sometimes molybdenum, are liberated at the cathode, whilst acetaldehyde and ethyl chloride are formed at the anode. By combination with an alcoholic calomel electrode, the electrolytic potential for molybdenum/molybdenum dichloride dissolved in alcohol has a value 0·552 volt referred to the hydrogen electrode as zero. In the potential series molybdenum falls between mercurous mercury and tervalent antimony. The alteration of the potential with dilution corresponds only qualitatively with Nernst's formula. D. F. T.

**Electric Nebulæ of Antipyretica.** H. ZWAARDEMAKER and H. ZEEHUISEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1272—1277).—The electric charge which is developed when a solution of an odorous substance in water is sprayed (Zwaardemaker, A., 1917, ii, 63; see also Backman, A., 1917, i, 498) is also produced by solutions of other substances, odorous or odourless, such as saponins, glucosides, alkaloids, antipyretica, and other physiologically active substances. In order to produce the electric phenomenon, the substance, added to water and sprayed with it, must satisfy certain conditions: (1) it must be soluble in water; (2) it must lower the surface tension; (3) it must volatilise when spread over a large evaporation area. Inorganic acids and salts, glycerol, sugars, dextrin, lecithin, and albumin do not produce the phenomenon.

A saturated aqueous solution of the antipyretic alkaloids, quinine, quinidine, cinchonine, cinchonidine, etc., sprayed under an over-pressure of 2 atmos., charges positively a screen at a distance of about 25 cm., the air around it and at some distance from it being charged negatively. The effect is less pronounced than that caused by odorous substances.

The charge produced by salicylic acid and its derivatives varies from zero in the case of insoluble phenyl and benzyl salicylates to a moderate effect with salts of salicylic acid and to effects caused by salicylic acid and its liquid derivatives, which are sometimes stronger than those due to typical odorous substances such as camphor. The salts owe their electrifying power to the anion; the cation lessens the charge of the nebula. The optimal electrifying power of salicylic acid is produced by a millinormal solution.

The third group of antipyretica examined comprises quinoline derivatives, pyrazoles, and *p*-aminophenols. The electric phenomenon is produced by pyramidone, phenacetin, and citrophen with moderate intensity, somewhat more strongly by kairine, and is extremely distinct in the case of antipyrine, salipyrine, acetopyrine, tussol, antifebrin, and euphorine.

To obtain normal results, the sprayer must be earthed. The magnitude of the electric charge is greatly affected by the addition of sucrose or sodium chloride to the solution. The charge is always increased by the former, but the effect of sodium chloride depends on its concentration. C. S.

**New Cryoscopic Tube and Method.** GIUSEPPE ODDO (*Gazzetta*, 1917, **47**, ii, 188—199).—The tube described and figured differs from the usual form in having a wide side-tube set obliquely to the main tube near the bottom of the latter. This tube is closed with a stopper, and is used for the rapid introduction of solvent and substance. The arrangement is intended more especially for working with very hygroscopic substances. R. V. S.

**Condition of Substances in Solution in Absolute Sulphuric Acid. VI.** G. ODDO and A. CASALINO (*Gazzetta*, 1917, **47**, ii, 200—232. Compare Oddo and Scandola, A., 1910, ii, 1035).—Continuing this investigation, the authors have studied the behaviour of thirty-one organic acids dissolved in absolute sulphuric acid. In the case of the monocarboxylic acids, such as *n*-butyric acid, the molecular weight observed is a little more than 50% of the true molecular weight, indicating that these acids form dissociated oxonium salts. Among the dicarboxylic acids, oxalic acid gives the highest values, exceeding 80% of the molecular weight, and the percentages observed increase with the concentration. The rest of the acids examined in this series have apparent molecular weights which are smaller the more distant the two carboxyls, and the figures obtained decrease with the concentration. The conclusions which may be drawn from the experimental data as to the constitution of solvent and solutes are discussed. R. V. S.

**Condition of Substances in Solution in Absolute Sulphuric Acid. VII.** G. ODDO and A. CASALINO (*Gazzetta*, 1917, **47**, ii, 232—243. Compare preceding abstract).—This paper deals with the behaviour of certain aldehydes, ketones, lactones, and anhydrides in absolute sulphuric acid. The aldehydes, ketones, and lactones behave like the monobasic acids described in the preceding paper. Acetic anhydride has 48·9—34·3% of its true molecular weight, succinic anhydride 89·1—68·4%, and phthalic anhydride 111·7—89·0%. The variations in each case correspond with varying concentrations. R. V. S.

**The Laws of the Vapour Pressures of Water and of other Vapours.** PIETRO ENRICO BRUNELLI (*Nuovo Cim.*, 1917, [vi], **14**, ii, 55—68).—The formula $\log p = 23{\cdot}08647 - 4{\cdot}5 \log T - 2980{\cdot}46/T - 0{\cdot}00278T + 0{\cdot}000002825T^2$, where $p$ is the pressure in mm. of mercury and $T$ is taken to be $273{\cdot}09 + t$, gives the vapour pressure of water more exactly and over a longer range of temperature than any of those hitherto proposed. Similar formulæ are given for carbon dioxide and ammonia, and in these cases also the agreement with observed values is satisfactory. R. V. S.

**The Saturated Vapour Pressures of Substances of High Atomicity.** E. ARIÈS (*Compt. rend.*, 1918, **167**, 267—270. Compare this vol., ii, 294).—The formula given for compounds containing more than eight atoms in their molecule is $\Pi = \tau^3 Z/x$, where

$x = \tau^2\Gamma$, and formulæ are given in the cases of pentane, hexane, heptane, and octane showing the variations of $\Gamma$ with the reduced temperature $\tau$. The calculated values are in fairly close agreement with those observed by Young for these four hydrocarbons.

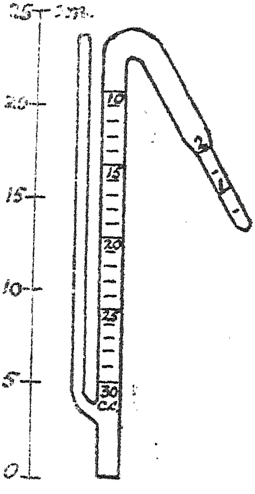
W. G.

**The Manipulation of Volatile Substances. III.** Alfred Stock (*Ber.*, 1918, **51**, 983—989. Compare A., 1917, ii, 442).—The following pieces of apparatus are described with diagrams, and an account is given of their applications.

I. An improved form of gas-holder for substances which can be condensed by liquid air (*ibid.*).

II. (*a*) An arrangement for filling a tube with a gas or mixture, without exposure to the air, and sealing it, for example, a mixture of hydrogen bromide, monosilane, $SiH_4$, and aluminium bromide, and (*b*) a simple device, "vacuum tube opener," for breaking the capillary of a sealed tube and leading off the gases it may contain without exposure to the air.

III. A simple apparatus for analysing a gaseous mixture by measuring the pressure of the gas left uncondensed at different temperatures, suitable for cases in which the uncondensable impurity is not more than 25%, and is, of course, insoluble in the liquefied gas. The construction of the apparatus is sufficiently clear from the annexed diagram, and it is used as follows. A suitable volume of the gas is admitted into the measuring tube over mercury, which is easily done without disturbing the column in the side-limb, this serving as a manometer. The open end is closed with a good stopper, and the constricted end is then immersed in the cooling bath, such as liquid air, and when the levels of the mercury columns are steady, the volume of the unabsorbed gas is read off and the pressure upon it found from the difference in the mercury levels. The temperature of the residual gas will not be uniformly the same as the initial gas, for part of it will be within the range of the cooling-bath. A sufficiently accurate correction may be made by noting the contraction in volume when the tube is filled with air and the constricted end is placed in the bath, the immersion being to the same depth as in an actual analysis. Having now corrected the initial and final volumes to *N.T.P.*, the determination of the proportion of unabsorbed gas is simple.



J. C. W.

**Thermochemical Studies.** Daniel Lagerlöf (*J. pr. Chem.*, 1918, [ii], **97**, 137—140).—As an extension of the earlier paper (this vol., ii, 62), it is shown that if Zubow's experimental values are corrected by a divisor 1·00888 instead of 1·007, as suggested by Roth, the results thus obtained for *n*-hexane and *n*-octane are almost identical with those calculated by the author. D. F. T.

**The Characteristic Equation of Fluids.** Pierre Weiss (*Compt. rend.*, 1918, **167**, 293—296. Compare this vol., ii, 291).—A mathematical discussion of the subject. W. G.

**The Characteristic Equation of Fluids.** Pierre Weiss (*Compt. rend.*, 1918, **167**, 364—366. Compare preceding abstract).—By combining the equation expressing the law of dilatation (*loc. cit.*) and the general equation $\Pi = a/v^{\eta}$ for the law of internal pressure, the characteristic equation of fluids becomes

$$(p + a/v^{\eta})(v - b) = \zeta RT,$$

where $a$, $b$, $\zeta$, and $\eta$ are constants, and $R$ is the constant of perfect gases. Very different combinations of these constants may occur for the same substance, but generally the values $\zeta = 1$ and $\eta = 2$ in the region of large volumes, and in that of high densities $\zeta$ is great and the co-volume is small. W. G.

**The Molecular Condition of Alloys in the Crystalline State and its Relation with the Form of the Equilibrium Diagram.** G. Masing (*Int. Zeitsch. Metallo.*, 1916, **9**, 21—37; from *Chem. Zentr.*, 1918, i, 703—704).—The idea of extensive dissociation in compounds which over a considerable range of concentration are able to form mixed crystals with the two components is not opposed to crystallographic or general considerations; indeed, from the point of view of the phase rule also, dissociation is possible in the solid state with such compounds as opposed to compounds which are unable to form mixed crystals. A compound which is largely dissociated in the solid state and is capable of taking only small quantities of the components into solid solution can, as an independent crystalline entity, possess a slight solvent power for the components only over a small temperature interval in the immediate neighbourhood of the temperature boundary of its area of existence, for example, of the m. p. A highly dissociated compound which forms mixed crystals with its components over a wide range of temperature must also give rise to homogeneous mixed crystals over a large interval of concentration. If, however, the crystalline form of a compound possessing very limited miscibility is stable in the solid state over a wide range of temperature, the compound can be only slightly dissociated, and the extent of the possible dissociation is proportional to the breadth of the area of existence of the homogeneous crystals. It is thus possible from the equilibrium diagram to draw a conclusion as to the molecular condition of an alloy, but the decision concerns only the upper limit of the degree of dissociation; an extensive range of solubility in the solid state is not trustworthy evidence of extensive dissociation.

With compounds which are strongly dissociated in the solid state, the maximum in a fusion or transformation curve need not correspond with the composition of the compound, and the same limitation holds also for other properties, such as conductivity and its temperature-coefficients. The maximum (or minimum) under such conditions is only an indication of the existence of a compound. These deductions are not applicable to compounds which are stable over a wide range of temperature without taking the components into solid solution. There is no symmetrical relationship between solubility curves and the curves of homogeneous equilibrium.

D. F. T.

**The Artificial Coloration of Spherolites with Helicoidal Winding (Tartrates and Hydrogen Malates).** PAUL GAUBERT (*Compt. rend.*, 1918, **167**, 368—370).—The spherolites are easily obtained, artificially coloured, if a solution of the substance containing some methylene-blue is evaporated as a thin layer on a glass plate. The temperature and velocity of crystallisation have a great influence on the production of these spherolites. The methylene-blue is in the crystalline state in the spherolites. Good results were obtained with ammonium hydrogen malate and the hydrogen tartrates of sodium, ammonium, rubidium, and thallium.

W. G.

**Chemical Studies on Physiology. V. "Soluble" and "Insoluble" Colloids, Genuine and Spurious Jellies, Protoplasma and Cell Permeability.** E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, **88**, 232—282).—A theoretical paper. The authors distinguish between "soluble" and "insoluble" colloids. They assume that in all cases of solution the solute forms combinations with many molecules of the solvent, and solutions with all stages between molecularly dispersed and colloidally dispersed particles exist. The latter form "soluble" colloids. In contradistinction to these, "insoluble" colloids exist, which owe their dispersion to the adsorption of substances on their surface with great affinity for water. To the latter class proteins belong. The view of the authors on these substances has been expressed in previous papers. Gelatin is regarded as a mixture of polypeptides polymerised by means of calcium salts. Jellies are formed from colloids with great power of combining with water, and come into existence when the whole of the water in the system is accumulated on the surface of the colloidal particles. Corresponding with the "soluble" and "insoluble" colloids are the "genuine" and "spurious" jellies, the former of which only are reversible. The authors discuss the application of their ideas to the problems of cell permeability and metabolism. S. B. S.

**Chemical Equilibria in the Reduction and Cementation of Iron.** RUDOLF SCHENCK (*Zeitsch. Elektrochem.*, 1918, **24**, 248—255).—A general résumé of work on the iron-carbon, iron-carbon monoxide, and similar equilibria. J. F. S.

**Propagation of Flame through Tubes of small Diameter.** WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1918, **113**, 656—666).—In continuation of previous experiments on the speed of the "uniform movement" during the propagation of flame in mixtures of methane and air, observations have been made with tubes of small diameter. The results obtained show the increased cooling effect of the walls of the tube as its diameter is decreased, in that the apparent limits of inflammability are narrowed considerably. It is also found that the speeds of the flames tend towards a constant value of about 35 cm. per second as the limiting mixtures are approached, and it is supposed that this represents the slowest speed at which continued propagation of flame (" uniform movement ") is possible in mixtures of methane and air.

Experiments made on the propagation of flame through tubes open at both ends, the mixture of methane and air in the tube being ignited near one end of the tube, show that the distance travelled before vibrations are set up which lead to the extinction of the flame depends on the length and diameter of the tube and on the composition of the mixture. The distance increases with the length and the diameter of the tube and diminishes as the percentage of methane in the mixture approaches that corresponding with the maximum speed of propagation of the flame (9·5—10% methane). In consequence of these relations, it follows that a length of tube the diameter of which is small enough to prevent the passage of flame in the mixture which corresponds with maximum speed of flame propagation may fail to do so when the mixture contains a smaller proportion of methane.

Further experiments described have reference to the propagation of flame through short lengths of narrow brass tubes from vessels filled with inflammable mixtures. The explosion vessels, consisting of tubes 2 cm. in diameter and of different lengths, contained 10% mixtures of methane and air. The mixture was ignited near the closed end, and the speed with which the flame reached the narrow brass exit tube was varied by varying the length of the explosion tube. The results obtained with brass tubes from 4 to 8 mm. in diameter, and with explosion vessels varying in length from 10 to 40 cm., show clearly that the increased speed of propagation of the flame reduces considerably the protection which is afforded by the narrow brass exit tubes. H. M. D.

**Relative Activities of Methyl, Ethyl, and *n*-Propyl Iodides with Sodium α- and β-Naphthoxides.** HENRY EDWARD COX (T., 1918, **113**, 666—674).—The rate of the reactions between the alkyl iodides and sodium α- and β-naphthoxide in ethyl-alcoholic solution has been measured at 40°. For equivalent quantities of the reacting substances, the course of the reaction is satisfactorily represented by the equation for a bimolecular change. The magnitude of the velocity-coefficient increases, however, with the dilution of the original solution. The coefficient $k_v$ for dilution $v$ can be expressed in the form $k_v = k_1 + a \log v$. This equation holds for ethyl and *n*-propyl iodides at least as far as $v=40$. For methyl iodide, the relation holds up to $v=10$ in the case of sodium α-naphthoxide and to $v=7$ for the β-naphthoxide. At higher dilutions, methyl iodide reacts more rapidly than would be expected from the empirical formula.

The reactivity of the iodides decreases with increase in the weight of the alkyl group. Sodium α-naphthoxide is more reactive than the β-compound. H. M. D.

**The Law of Action of Sucrase: Hypothesis of an Intermediate Compound.** H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1918, **167**, 338—341).—When the sucrose is in excess with respect to the sucrase, the weight $x$ of sugar hydrolysed in a time $t$ is proportional to the quantity of sucrase $n$ and independent of the initial concentration $a$ of the sucrose. The velocity of inversion, at first constant, diminishes until the excess of sucrose has disappeared, at which point the value of the quotient $(dx/dt)/(a-x)$ remains constant. If, on the other hand, the sucrase is in excess with respect to the sucrose, the rate of inversion is proportional to $a$ and independent of $n$, and the velocity of hydrolysis, constantly decreasing, is such that the quotient $(dx/dt)/(a-x)$ remains constant throughout. These results are in accord with Brown's hypothesis as to the formation of a compound between the sugar and the enzyme (compare T., 1902, **81**, 373). W. G.

**Influence of Foreign Substances on the Activity of Catalysts. V. Experiments with Palladium Hydrosol in the Presence of the Hydroxides of Iron, Copper, and Zinc.** C. PAAL and WILHELM HARTMANN (*Ber.*, 1918, **51**, 894—906. Compare this vol., ii, 303).—Ferric hydroxide is peptised to a certain extent by sodium protalbinate, but the amount of iron taken up is lessened by the addition of sodium hydroxide. Freshly precipitated ferric hydroxide does not hinder the catalysis of mixtures of hydrogen and oxygen by palladium hydrosol, protected by sodium protalbinate, nor does it suffer reduction under such conditions.

Cupric hydroxide is taken up by sodium protalbinate to a fairly considerable extent, and free sodium hydroxide enhances the peptisation. More concentrated cupric hydroxide hydrosols than have hitherto been described can therefore be made (compare A., 1906, ii, 358). Freshly precipitated cupric hydroxide lowers the activity of palladium hydrosol towards hydrogen and oxygen mixtures, but large quantities would be necessary to spoil the catalyst entirely. With colloidal cupric hydroxide, however, the activity of the catalyst actually increases for a time, but then falls off rather rapidly. In both cases the falling off is not regular, for after some time a slight recovery sets in, followed again by further loss of activity.

Zinc hydroxide is also peptised by sodium protalbinate. This depresses the activity of palladium hydrosol during the first hour of an experiment to about half the normal, but a remarkable recovery then sets in, and the catalyst actually becomes slightly more active than usual, although it still contains colloidal zinc hydroxide. J. C. W.

**Inhibition of Foaming.** Cyrus H. Fiske (*J. Biol. Chem.*, 1918, **35**, 411—413).—From a consideration of the manner of action of substances which inhibit foaming, the author draws the conclusion that the chief properties contributing to the efficiency of an organic liquid as a foam inhibitor are as follows: high surface activity, high surface tension, high interfacial tension, low solubility, and low volatility. A substance which possesses these characteristics is *iso*amyl *iso*valerate (or a mixture of this substance with *iso*amyl alcohol). To prepare the reagent, 28 c.c. of anhydrous *iso*valeric acid, 30 c.c. of *iso*amyl alcohol, and 1 c.c. of concentrated sulphuric acid are boiled together for one hour under a reflux condenser. The resulting ester is carefully freed from acid by shaking with sodium carbonate and then well washed with water. It may be used at once or after distillation. An alternative method of preparation is to oxidise *iso*amyl alcohol with potassium dichromate and sulphuric acid; the product contains some *iso*valeraldehyde, which can, however, be removed by shaking with sodium hydrogen sulphite solution. H. W. B.

**A Simple Gas Generator.** Bruck (*Chem.-techn. Woch.*, 1917, **1**, 246; from *Chem. Zentr.*, 1918, i, 690).—A small generator working on the same principle as Kipp's apparatus is constructed from a wide glass tube by fitting it internally near its closed end with a perforated shelf of rubber or similar material. The neck of the tube is fitted with a cork; through this passes a test-tube to which has been sealed concentrically a narrow glass tube, this glass tube reaching through the shelf to the bottom of the wide containing tube. For the generation of hydrogen, zinc is placed on the shelf and hydrochloric acid introduced at the mouth of the test-tube; the acid flows through the test-tube and its extension into the end of the wider tube, and then rises until it passes through the shelf to the zinc. D. F. T.

**Aspirator.** J. M. Johlin (*J. Ind. Eng. Chem.*, 1918, **10**, 632).—A large glass bottle, serving as the reservoir, is closed by a cork carrying three tubes; one of these is the inlet or outlet for the gas, another is used as a siphon for emptying the water from the bottle when this is full, whilst water is admitted through the third tube so that the gas may be forced out. The water enters through a narrow jet in a wide tube fitted at the top of the third tube, the wide tube being provided with a side-tube which carries off any excess of water. W. P. S.

**Safety Valve.** E. Rittenhouse (*J. Ind. Eng. Chem.*, 1918, **10**, 633).—A short length of glass tube has a small bulb at its lower end and a narrow central tube is sealed to the inner wall and extends almost to the bottom of the bulb; a globule of mercury in the bulb seals the lower end of the central tube. When this piece of apparatus is inserted in a hole in a cork closing a flask, air may enter through the central tube, bubble through the mercury, and enter the flask through a small opening in the wall of the tube above the bulb. The valve is useful when ammonia is being distilled and absorbed in standard acid; air is admitted to the flask during any temporary decrease in pressure in the latter, thus preventing the standard acid from being drawn into the flask. Vapours cannot escape through the valve outwards owing to the mercury rising in the central tube. W. P. S.

**Filtration Apparatus.** F. Härtel (*Zeitsch. Nahr. Genussm.*, 1918, **35**, 444—445).—An apparatus for filtration under reduced pressure consists of a rectangular specimen jar without a neck and having a square, overlapping lid. The jar is laid on its side, and in the upper side are bored two holes, one for receiving the stem of a funnel or filter tube and the other a tube provided with a three-way tap and connected with a pump. The vessel (beaker, flask, etc.) in which the filtrate collects is placed in the jar beneath the stem of the funnel. The apparatus enables the filtrate to be collected directly in a vessel, in which it may be subjected to any further treatment, and transference from a filter-flask is avoided.

W. P. S.

**Ultra-filtration of Small Quantities of Liquid by Centrifugal Force.** D. J. de Waard (*Arch. Néerland. Physiol.*, 1918, **2**, 530—533).—The apparatus consists of a thick glass tube about 60 cm. long and 1 cm. bore separated from a similar tube, closed at its distal end, by a nickel disk pierced with openings about 2 mm. in diameter. The membrane is placed on the disk, and then the tubes are pressed firmly on to the disk by means of a screw cap and collars attached to the tubes. The whole apparatus now resembles a test-tube divided into an upper and a lower portion by the disk supporting the membrane. A minute hole is pierced in the side of the lower tube just below the collar to allow of the escape of air. The liquid to be filtered is poured on the membrane, and the apparatus then placed in a centrifugal machine. If the number of revolutions per minute is about 3000, the filtration pressure is about 6 atmospheres per sq. cm. The membrane may be of animal origin, or prepared from celloidine or other material by Walpole's method. During centrifugalisation, the lower tube should be protected by an outer tube of copper, the intervening space being filled with oil. H. W. B.

**New Form of Ultra-filter. Some of its Uses in Biological and Synthetic Organic Chemistry.** Philip Adolph Kober (*J. Amer. Chem. Soc.*, 1918, **40**, 1226—1230).—Quantitative dialysis has hitherto been impossible on account of the extreme dilution of both filtrate and residue caused by the dialysing water. Through the discovery that all semipermeable membranes pervaporate (Kober, A., 1917, ii, 295), the difficulties of ultra-filtration by dialysis have been completely overcome. An apparatus, consisting essentially of a dialyser with automatic water supply connected by a siphon to a pervaporator, is figured and described. Its action depends on pervaporating both the dialysate and the diffusate solutions during dialysis, whereby quantitative dialysis is rendered possible.

The author gives a few examples showing that in biological or synthetic work humus material or highly coloured by-products, which cannot be removed by charcoal, are rapidly or completely removed by ultra-filtration. [See also *J. Soc. Chem. Ind.*, October.]
C. S.

**Device to ensure Tight Connections between Glass and Rubber Tubing.** C. C. Kiplinger (*J. Ind. Eng. Chem.*, 1918, **10**, 631).—A piece of stout string is tied round the joint and is tightened by slipping a piece of metal wire between the string and rubber, and twisting the wire until the string is quite tight; the ends of the wire are then bent round the tube. W. P. S.

## Inorganic Chemistry.

**Enrichment of Iodine during its Purification.** Francesco Lenci (*Boll. chim. farm.*, 1918, **57**, 121—123).—In the purification of iodine, sublimation removes most of the cyanogen iodide, which sublimes first, and also the bromine and moisture, and sublimation in presence of potassium iodide gets rid of chlorine and bromine. Loss of iodine during the purification may be avoided by treatment based on the results obtained by Tarugi (this vol., ii, 203). [See, further, *J. Soc. Chem. Ind.*, 579a.] T. H. P.

**The Theory of Transmission of Oxygen.** Ed. Justin-Mueller (*J. Pharm. Chim.*, 1918, [vii], **18**, 17—18).—Certain metallic salts, particularly copper salts, behave as anaeroxydases, and the authors conclude that these substances have secondary valencies having the power to take up oxygen and to transmit it at once under suitable conditions. Anaeroxydases and copper salts behave alike in the oxidation of guaiacum resin in the presence of hydrogen peroxide. W. P. S.

**Reduction of Sulphuric Acid by Carbon Monoxide.** Jar. Milbauer (*Chem. Zeit.*, 1918, **42**, 313—315).—At 250°, sulphuric acid is reduced by carbon monoxide according to the equation

$H_2SO_4 + CO = CO_2 + SO_2 + H_2O$; about 25 mg. of sulphur dioxide are produced per hour when carbon monoxide is passed at the rate of 0·6 litre per hour through a layer of sulphuric acid 9·5 cm. in height. The reaction proceeds as long as the strength of the sulphuric acid does not fall below 91%, and is accelerated by the presence of certain catalysts, such as palladium, iridium, mercury, selenium, silver, gold, tin, etc. Platinum, osmium, and copper sulphate do not affect the rate of the reaction. W. P. S.

**Preparation and Testing of Pure Arsenious Oxide.** ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1918, **10**, 522—524).—Ordinary arsenious oxide is boiled for about one hour with a quantity of water insufficient to dissolve the whole of it, the solution filtered while hot, the filtrate concentrated until arsenious oxide begins to precipitate, and the solution again filtered. The separated oxide is tested for antimony by dissolving a portion in ammonia, adding hydrogen sulphide, boiling the mixture, and then cooling in ice-water; a turbidity is obtained if more than 0·15% of antimony trioxide is present, and in such case the arsenious oxide must be treated further as described. The purification depends on the fact that antimony, if present, is absorbed almost completely by the solid arsenious oxide which remains undissolved in the aqueous solution. The final crystallisation of the pure arsenious oxide is best made from a slightly hydrochloric acid solution, and the product is then sublimed. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**Silicon Hydrides. V. Decomposition of Silicon Hydrides by Water. Action of Hydrogen Bromide on Monosilane.** ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1918, **51**, 989—996. Compare A., 1916, ii, 319; this vol., ii, 110, 111).—In the first communication on the silanes, it was reported that they suffer decomposition into silicic acid and hydrogen when left for a few hours in contact with water. It is now found that this reaction is largely conditioned by the alkalinity of the glass apparatus, for in quartz vessels, or with slightly acidified water practically no change takes place during several days.

This stability of the hydrides may be made use of in analysing mixtures of the three gases, monosilane, hydrogen bromide, and bromomonosilane. The last-named gas reacts immediately with water to form the gas disiloxane and hydrobromic acid, thus: $2SiH_3Br + H_2O = (SiH_3)_2O + 2HBr$. After two or three hours, the new gas reacts further to give hydrogen, thus: $(SiH_3)_2O + H_2O = SiO_2 + 3H_2$. If the volume of the mixture is $a$ c.c., the volume after the initial contraction is $b$ c.c., and the final volume after the production of hydrogen is $c$ c.c., then $c - b$ gives the volume of $SiH_3Br$ and $a - b - \frac{1}{2}(c - b)$ the volume of HBr.

From the point of view of carbon chemistry, a remarkable reaction of the silicon hydrides has now been discovered. Monosilane, for example, reacts very readily with hydrogen bromide in the presence of aluminium bromide, according to the equations $SiH_4 + HBr = SiH_3Br + H_2$, $SiH_4 + 2HBr = SiH_2Br_2 + 2H_2$, etc. In one experiment, which is fully described, 207 c.c. of monosilane and 188·8 c.c. of hydrogen bromide were heated for three hours at 100° in a sealed tube of 700 c.c. capacity, on the walls of which a little aluminium bromide had been deposited by sublimation, when 86·7 c.c. of monosilane, 52·5 c.c. of $SiH_3Br$, and 67·8 c.c. of $SiH_2Br_2$ were obtained from the product, practically all the hydrogen bromide having disappeared. This method is consequently better than direct bromination for the preparation of the lower bromides.

The apparatus employed is described in another paper (see this vol., ii, 353). J. C. W.

**Melting Points of Cristobalite and Tridymite.** J. B. FERGUSON and H. E. MERWIN (*Amer. J. Sci.*, 1918, [iv], **46**, 417—426).—Cristobalite prepared by heating clear quartz crystals for 144 hours at 1300—1400° melts at 1710°±10°.

Tridymite grains selected from the cristobalite mass were converted into cristobalite at 1667—1677° without melting. Two specimens of natural tridymite (one from Nevada and one from Mexico) both melted sharply at 1670°±10°. The results confirm those of Fenner (A., 1913, ii, 133), showing that the region of stability of cristobalite is above that of tridymite. [See, further, *J. Soc. Chem. Ind.*, 546A.] A. B. S.

**A Supposed Fusion of Carbon by O. Lummer.** M. LA ROSA (*Gazzetta*, 1917, **47**, ii, 19—31).—The author criticises Lummer's conclusions (*Verflüssigung der Kohle*, etc., Braunschweig, July, 1914), and directs attention to some of his earlier experiments. T. H. P.

**Residual and Extinctive Atmospheres of Flames.** THOMAS FRED ERIC RHEAD (*J. Soc. Chem. Ind.*, 1918, **37**, 274—278T).—Experiments have been made with the flames of a number of different gases to determine the amount of oxygen in (1) the "residual atmosphere," that is, the atmosphere in which the flame, burning in a limited supply of air, becomes extinguished, and (2) the "extinctive atmosphere," that is, the mixture of oxygen and nitrogen which is just unable to support combustion of the gas.

The residual atmospheres of flames of the hydrocarbons methane, propane, butane, and pentane were found to contain from 15·6% to 16·4% of oxygen, the value increasing gradually with the molecular weight. For cyanogen, the value found was 15·3%, for carbon monoxide 10·2%, and for hydrogen 5·7%. The oxygen content of the residual or extinctive atmosphere depends primarily on the rate of diffusion of the combustible gas into the atmosphere and on the complexity of the combustion process. Hydrogen, with a high rate of diffusion, a simple reaction, and a high initial rate of flame propagation in air, therefore leaves an atmosphere with a low oxygen content.

For the examination of the extinctive atmospheres, a novel experimental method was devised, consisting in feeding a flame with a mixture of air and nitrogen which could be varied at will with considerable nicety. The mixture which just extinguished the flame was taken as the extinctive atmosphere. The oxygen content in the case of the hydrocarbons methane to pentane was found to be practically constant at 16·3—16·6%, with a constant speed of the gas stream and of the current of air–nitrogen mixture. It was found, however, that the flame would continue to burn in an atmosphere containing less oxygen when the atmosphere was supplied at a greater speed. Coal gas behaves differently from a pure gas, on account of the widely different extinctive atmospheres of its two principal constituents, hydrogen and methane. Experiments on a mixture of these gases showed that in the presence of an atmosphere of low oxygen content the hydrogen burns preferentially. The methane under these conditions acts mainly as a diluent, and this accounts for the observation that in the case of coal gas the oxygen content of the extinctive atmosphere is diminished by increasing the speed of the gas stream. E. H. R.

**The Ternary System—Sodium Sulphate, Ammonium Sulphate, and Water. The Utilisation of Nitre Cake for the Production of Ammonium Sulphate.** Harry Medforth Dawson (T., 1918, **113**, 675—688).—An account is given of the equilibrium relations in the system $Na_2SO_4$–$(NH_4)_2SO_4$–$H_2O$ at temperatures between −20° and 100°. The characteristic features of the system, which are illustrated by diagrams of a somewhat novel type, are largely determined by the formation of the ternary compound $Na_2SO_4,(NH_4)_2SO_4,4H_2O$, which may exist in contact with solutions at any temperature between −16° and 59·3°. Below −16°, the double salt, in contact with solution, is decomposed, with the formation of Glauber's salt and ammonium sulphate, and above 59·3° it decomposes with the formation of the anhydrous simple salts. Other invariant temperatures are −19·5°, at which Glauber's salt, ammonium sulphate, and ice co-exist in equilibrium with saturated solution, and 26·5°, at which the saturated solution is in equilibrium with Glauber's salt, anhydrous sodium sulphate, and the double salt.

The curves which show the influence of temperature on the composition of the solutions saturated with respect to two solid phases are distinguished by the fact that the solutions saturated with respect to Glauber's salt and the double salt show a rapid diminution in the ammonium sulphate concentration and a rapid increase in the sodium sulphate concentration as the temperature rises from −16° to 26·5°. On the other hand, solutions saturated with respect to anhydrous sodium sulphate and the double salt show a decrease in the sodium sulphate concentration and a remarkably rapid increase in the ammonium sulphate concentration as the temperature rises from 26·5° to 59·3°.

Between −16° and 20°, the double salt is decomposed by water with the separation of Glauber's salt, and between 41·5° and 59·3° it is similarly decomposed with the separation of anhydrous sodium sulphate. These intervals of temperature represent the lower and upper transition intervals.

In virtue of the considerable differences in the values of the ratio of ammonium sulphate to sodium sulphate in the saturated solutions at high and low temperatures, it is possible to separate these salts by crystallisation under suitably controlled conditions. A method has been devised in which solutions of appropriate concentration are cooled to a temperature of about −10°, when Glauber's salt separates out, the mother liquors being subsequently evaporated at about 100° when pure ammonium sulphate is deposited until the ratio of ammonium sulphate to sodium sulphate in the hot solution has fallen to a value much smaller than that characteristic of the mother liquor from the crystallisation process.

H. M. D.

**Composition of Lime-Sulphur Solutions.** O. B. Winter (*J. Ind. Eng. Chem.*, 1918, **10**, 539—545).—Lime-sulphur solution which has been prepared from ordinary commercial lime and sulphur, and has been kept for several days, does not contain any appreciable amount of hydrogen sulphide, calcium hydrosulphide, calcium hydroxyhydrosulphide, or the corresponding salts of other metals; free calcium hydroxide is not present. When, however, an excess of lime has been used in preparing the lime-sulphur solution, or when the latter has been diluted with lime-water, free calcium hydroxide may be present for a time, but gradually disappears. The addition of magnesium sulphate to lime-sulphur solution produces a slight increase in the monosulphide sulphur and sulphide sulphur contents, whilst the thiosulphate sulphur content is not affected; the magnesium replaces calcium, magnesium polysulphide being formed and calcium sulphate crystallising from the solution. Free sulphur does not appear to be present in lime-sulphur solution, and any sulphur which separates is derived from the higher polysulphides. The orange-red crystals which separate from concentrated lime-sulphur solution have the composition $2CaO,CaS_3,11H_2O$, but it is improbable that they exist in this form in the solution. [See, further, *J. Soc. Chem. Ind.*, October.]

W. P. S.

**Influence of the Temperature of Burning on the Rate of Hydration of Magnesium Oxide.** Edward de Mille Campbell (*J. Ind. Eng. Chem.*, 1918, **10**, 595—596).—When magnesite is ignited at or below 1100°, the resulting magnesium oxide, when immersed in water, is hydrated completely within three months; if the ignition is made at 1450°, only 70% of the magnesium oxide is hydrated in six years. These results show that materials containing free magnesium oxide, if ignited at temperatures approaching that used in the production of Portland cement, will not be hydrated completely, even when immersed continuously in water, until after the lapse of twenty years or more. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**The Ternary Systems Lead-Bismuth-Silver and Lead-Gold-Silver.** MASAHARU GOTO (*J. Coll. Eng. Tokyo*, 1918, **9**, 63—114).—In the system lead–gold–silver, no ternary eutectic occurs. The temperature of the eutectic falls continuously from 350° for the lead–silver alloys to 208° for the lead–gold ones. The presence of gold reduces the power of silver of holding lead in solid solution. No compound is present. In the lead–bismuth–silver system, a ternary eutectic occurs containing 0·2% Ag, 43·6% Pb, and 56·2% Bi, which melts at 120°. Solid solutions occur in a narrow area around the silver corner of the diagram. F. C. TH.

**Compounds of Lead Fluoride and Chloride with Lead Phosphate.** M. AMADORI (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 143—148).—The results obtained in the thermal study of the system lead fluoride–lead phosphate (A., 1913, ii, 216) were vitiated, owing to the presence in the phosphate both of a slight excess of lead oxide and apparently also of traces of another substance the nature of which was not determined. The examination of this system has now been repeated, the lead phosphate used being prepared from the calculated quantities of lead oxide and pyrophosphate, the latter itself being obtained by precipitation of lead nitrate with disodium hydrogen phosphate. The results show that fused mixtures of lead orthophosphate and fluoride form, on solidification, the compound $Pb_3(PO_4)_2,PbF_2$, which solidifies at 1098°. This compound and the analogous chloropyromorphite, $Pb_3(PO_4)_2,PbCl_2$, solidifying at 1156°, correspond in composition with the mineral pyromorphite and undergo no transformation during cooling. Each of these compounds exhibits little if any miscibility with its components. T. H. P.

**Action of Hydrogen Sulphide on Mercuric Bromide.** GIAMBATTISTA FRANCESCHI (*Boll. chim. farm.*, 1918, **47**, 221—223).—The addition of a few drops of an alcoholic solution of hydrogen sulphide to an alcoholic solution of mercuric bromide produces slight milkiness, mercurous bromide and sulphur being formed: $H_2S + 2HgBr_2 = Hg_2Br_2 + S + 2HBr$. Addition of a greater proportion, but not an excess, of the hydrogen sulphide solution causes the precipitation of the canary-yellow double salt,

$$2HgS,HgBr_2 \quad (?Hg[S \cdot HgBr]_2),$$

whilst when excess is added, black mercuric sulphide is precipitated. The successive reactions are represented by the equations: (1) $H_2S + 2HgBr_2 = Hg_2Br_2 + S + 2HBr$; (2) $H_2S + 3Hg_2Br_2 + 3S = 2(2HgS,HgBr_2) + 2HBr$; (3) $H_2S + HgS,HgBr_2 = 2HgS + 2HBr$.

T. H. P.

**Recovery of Molybdic Acid.** W. H. LYNAS (*Met. and Chem. Eng.*, 1918, 169).—The following method is suggested for recovering molybdic acid from the filtrates from phosphorus estimations. To the boiling filtrates from 3500 c.c. of ammonium molybdate solution, 200 grams of commercial sodium phosphate are added. The precipitate is washed by decantation and dried on a sand-bath; it is then dissolved in ammonia and the phosphorus precipitated by the addition of magnesium nitrate solution and filtered. The volume of the filtrate is made up to 3500 c.c. by the addition of 1900 c.c. of 1:1 nitric acid. [See, further, *J. Soc. Chem. Ind.*, October.] F. C. Th.

**Bismuth Tellurides. II.** M. Amadori (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 131—134. Compare A., 1915, ii, 783).—The author has subjected to thermal investigation that part of the Bi–S–Te system comprising the compositions of other natural sulpho-tellurides, that is, $Bi-Bi_2Te_3-Bi_2S_3$. It is found that the single components, Bi, $Bi_2S_3$, and $Bi_2Te_3$, and the compound, $Bi_2S_3,Bi_2Te_3$, separate out from fused mixtures either in the pure state or in simple eutectic mixtures; there is no formation of new compounds and no miscibility relationships between these substances. No phenomena are observed which are attributable to the formation of substances analogous to tetradimite, grunlingite, or joseite. T. H. P.

## Mineralogical Chemistry.

**Anhydrite in the Boulders carried by the Lava of Stromboli.** G. Ponte (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 348—350).—The mineral has the percentage composition:

| CaO. | $SO_3$. | BaO. | SrO. | $SiO_2$. | $Fe_2O_3$. |
|---|---|---|---|---|---|
| 42·09 | 57·79 | 0·04 | 0·06 | traces | 0·02 |

R. V. S.

## Analytical Chemistry.

**Calculation of Analytical Results.** J. Grossfeld (*Chem. Zeit.*, 1918, **42**, 389—391).—Tables are given showing the equivalents and analytical factors of a large number of elements, inorganic compounds, organic compounds, and acids, sugars, alkaloids, etc. W. P. S.

**Graphic Methods of Analysis.** HANS GRADENWITZ (*Chem. Zeit.*, 1918, **42**, 368).—The system of curves suggested previously by the author (this vol., ii, 245) merely indicates the application of this method of analysis; no claim is made for priority or for the particular trustworthiness of the diagrams given.
W. P. S.

**Graphic Methods of Analysis.** WA. OSTWALD (*Chem. Zeit.*, 1918, **42**, 367—368).—The author recommends the use of Gibb's triangular scheme for plotting the curves employed in the estimation of the composition of ternary mixtures; this system is simpler and more trustworthy than that described by Gradenwitz (this vol., ii, 245, and preceding abstract). W. P. S.

**Use of the Dipping Refractometer.** WYATT W. RANDALL (*J. Ind. Eng. Chem.*, 1918, **10**, 629—630).—In using the immersion refractometer, the author has found that the temperature of the liquid under examination rises slightly when the metal cup containing the liquid is attached to the instrument, probably due to the conduction of heat from the air to the cup through the metal parts of the instrument. Untrustworthy readings are therefore obtained. This heating does not take place when small beakers are used in place of the metal cups. W. P. S.

**New Form of Colorimeter.** JOSEPH C. BOCK and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1918, **35**, 227—230).—The new colorimeter differs from the Duboscq instrument in having only one plunger, the light from a mirror being thrown partly through the glass containing the liquid the colour intensity of which it is required to measure, and partly through a cell containing a known depth of liquid of standard colour. H. W. B.

**Use of the Interferometer in Gas Analysis.** F. M. SEIBERT and W. C. HARPSTER (*U.S. Bureau of Mines, Tech. Paper*, No. 185, 1918, 18 pp.).—A description of the application of the Rayleigh interferometer to gas analysis, especially in special work necessitating frequent analyses. Using a gas chamber 1 metre long, the precision is equivalent to the ordinary volumetric gas analysis made over mercury.

The accuracy of the measurements depends largely on the length of the gas chambers, and the refractive index must be measured with great precision for accurate work. The percentage error made in determining one component of a mixture depends also on the choice of a comparative gas, and it is found better to calibrate the instrument empirically against some exact analytical method.

In order to obtain an accuracy of 0·02%, when using as a gas of comparison the gas that predominates in the mixture, the absolute refraction coefficients should differ by about 0·0001; therefore the greater the difference of the coefficients of absolute refraction, the greater is the accuracy of the method. The gases compared must be dry and at the same temperature. [See, further, *J. Soc. Chem. Ind.*, 608A.] C. A. K.

**Electrical Conductivity Recorder for Salinity Measurements.** E. E. WEIBEL and A. L. THURAS (*J. Ind. Eng. Chem.*, 1918, **10**, 626—627).—The apparatus described gives a continuous record of the salinity or density of a solution by the measurement of its electrical conductivity; it may be used for the concentration of brines and other salt solutions, and also many other substances the composition of which is constant during changes in concentration. Two electrolytic cells are used and are connected with a suitable alternating current galvanometer and a recorder. Temperature compensation is effected by placing both cells, which are in the two arms of a Wheatstone bridge, in a uniform temperature-bath or directly in the solution under examination. W. P. S.

**A New Physico-chemical Volumetric Method.** RENÉ DUBRISAY (*Ann. Chim.*, 1918, [ix], **9**, 25—48).—The method described for determining the acidity of a solution is based on the observation and measurement of the tension at the surface of separation of two non-miscible liquids. A definite volume of vaselin oil mixed with 2% of oleic acid is allowed to flow slowly into a known volume of the liquid under examination from a jet just plunged into it, and the number of drops formed is counted. This is repeated after the addition of known volumes of standard alkali, and it is found that there is a sudden rise in the number of drops formed at the point of neutralisation. The vaselin oil may be replaced by a solution of stearic acid in benzene. W. G.

**Decanting.** H. TILLISCH (*J. Ind. Eng. Chem.*, 1918, **10**, 631).—The time required for a precipitate to settle is shortened considerably if the test-tube is inclined at an angle of 45°. W. P. S.

**Neutralisation of Hydrogen Peroxide by Sodium Borate.** J. CAMBE and H. DIACONO (*J. Pharm. Chim.*, 1918, [vii], **18**. 12—17).—The presence of small quantities of hydrofluosilicic acid or hydrofluoric acid in hydrogen peroxide inhibits the formation of a red coloration when the peroxide is treated with phenolphthalein and an excess of sodium borate; freshly prepared hydrogen peroxide, which contains "active oxygen," also fails to give a red coloration when treated with an excess of sodium borate in the presence of phenolphthalein. Other indicators are not affected by the above-mentioned substances. W. P. S.

**Estimation of Chlorine in Presence of Silicates.** G. BRUHNS (*Zeitsch. angew. Chem.*, 1918, **31**, [i], 156).—In estimating chlorine in mixtures containing silicic acid, it is unnecessary to render the silica insoluble and separate it by filtration. Mohr's method of titrating the chlorine with silver nitrate is trustworthy provided that the liquid be made neutral to phenolphthalein by means of nitric acid, and any gelatinous silicic acid be finely distributed throughout the liquid. C. A. M.

**Source of Error in Bunsen's Method for the Estimation of Peroxides, Chlorates, etc.** E. Rupp (*Zeitsch. anal. Chem.*, 1918, **57**, 226—230).—When manganese dioxide, potassium chlorate, etc., are estimated by distilling the substance with hydrochloric acid, collecting the distillate in potassium iodide solution, and titrating the liberated iodine, the results obtained are from 0·5% to 2% too low. The error varies with the conditions of the distillation, and is due to reaction between chlorine and water vapour, hydrochloric acid and oxygen being formed. Fairly trustworthy results are, however, obtained if potassium iodide is added to the distillation mixture and the iodine then distilled, collected, and titrated. In some cases, where the hydrochloric acid is too concentrated, iodine in small amount is liberated from the potassium iodide by the action of the acid. W. P. S.

**Estimation of Sulphuric Acid and Barium as Barium Sulphate.** Z. Karaoglanow (*Zeitsch. angew. Chem.*, 1918, **31**, 160).—A criticism of an investigation recorded by Winkler (*Zeitsch. angew. Chem.*, 1917, **30**, 301—303) on the gravimetric estimation of sulphuric acid and barium. The author has shown recently (this vol., ii, 47) that potassium salts influence the results, and that the presence and concentration of the hydrochloric acid, the time of precipitation, temperature, all have an effect on the precipitation of the barium sulphate. There is no evidence that barium hydrogen sulphate is formed during the precipitation.
W. P. S.

**The Microchemical Estimation of Nitrogen.** Ivar Bang (*Biochem. Zeitsch.*, 1918, **88**, 416—419).—A reply to some criticisms of Schollema and Hitterschy (*ibid.*, 1917, **84**, 354, 371).
S. B. S.

**Use of Sodium Sulphate in the Kjeldahl-Gunning Method.** C. T. Dowell and W. G. Friedeman (*J. Ind. Eng. Chem.*, 1918, **10**, 599—600).—The authors find that sodium sulphate (either anhydrous or an equivalent quantity of the crystallised salt) is as effective as is potassium sulphate in the digestion part of the Kjeldahl-Gunning method. W. P. S.

**Estimation of Ammonia in Urine.** A. Leclère (*Compt. rend. soc. biol.*, 1917, **80**, 959—962; from *Physiol. Abstr.*, 1918, **3**, 262).—By distilling urine with lithium carbonate, ammonia is rapidly and quantitatively liberated. The hydrolysing action on urea and amino-acids is slight, so that only a small correction is necessary. S. B. S.

**Ammonia and Nitric Nitrogen Estimations in Soil Extracts and Physiological Solutions.** B. S. DAVISSON (*J. Ind. Eng. Chem.*, 1918, **10**, 600—605).—Ammonia nitrogen is estimated by the aeration method at the ordinary temperature in the presence of magnesium oxide or sodium carbonate; the ammonia is absorbed in acid towers, and the contents of the latter are distilled subsequently with magnesium oxide in the usual way. The residual liquid in the aeration flask is then acidified with sulphuric acid, heated, cupric hydroxide added, the mixture filtered, the filtrate boiled for thirty minutes with the addition of sodium hydroxide, and the nitrate reduced with Devarda's alloy, the resulting ammonia being estimated by distillation. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**The Estimation of Nitrites.** F. DIENERT (*Compt. rend.*, 1918, **167**, 366—367).—The method is based on the reaction $NaNO_2 + 2HI = NaI + I + NO + H_2O$. Three flasks, (1) containing 50 c.c. of 4% potassium iodide, (2) containing 10 c.c. of *N*-sulphuric acid, (3) containing the solution of the nitrite, are connected in the order mentioned, and carbon dioxide passed through them until all air is displaced. The contents of (1) are then driven over into (2), and this mixture in turn into (3). Ten c.c. of a 20% solution of ammonium carbonate are then added, and the free iodine titrated by means of *N*/70-arsenious acid, of which 1 c.c. = 0·2 mg. of nitrous nitrogen. Care must be taken to avoid the entrance of oxygen into flask (3) until the liquid has been made alkaline by the addition of the ammonium carbonate. W. G.

**Colorimetric Estimation of Phosphoric Acid in Potable Water.** P. N. VAN ECK (*Pharm. Weekblad*, 1918, **55**, 1037—1040).—The hydrazine sulphate employed in Riegler's colorimetric method for estimating phosphoric acid can be replaced by stannous chloride, the same blue coloration being produced. A. J. W.

**Estimation of Zeolitic Silicic Acid in Soils.** K. K. GEDROITZ (*Reprint*, pp. 400—406).—The method commonly used in Russian laboratories for the estimation in soils of so-called zeolitic silicic acid, that is, silicic acid liberated when the soil is treated with concentrated hydrochloric acid in the hot, is tedious, and the author now describes a new method, which is rapid and does not necessitate the use of large platinum dishes. The results obtained by this method approximate closely to those given by the old method. T. H. P.

**Pressure Method for the Estimation of Carbon Dioxide in Carbonates.** W. H. CHAPIN (*J. Ind. Eng. Chem.*, 1918, **10**, 527—529).—The carbonate is dissolved in dilute hydrochloric acid contained in a flask of known capacity; the flask is provided with a small mercury manometer, and the weight and percentage of the carbon dioxide are calculated from the change in pressure. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**The Bisulphate Method of Estimating Radium.** HOWARD H. BARKER (*J. Ind. Eng. Chem.*, 1918, **10**, 525—527).—In this method, the mineral is fused and boiled with a mixture of sodium and potassium hydrogen sulphates, and the emanation is passed into the ionisation chamber of an electroscope. Readings of the rate of discharge are made three hours after the introduction of the gas. When the mineral under examination contains thorium, the gas cannot be transferred directly to the electroscope during fusion, but must be collected in a gas burette to allow the thorium emanation to decay. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**Methods of Estimating Potassium.** A. VÜRTHEIM (*Chem. Weekblad*, 1918, **15**, 827—842).—A critical survey of the literature of the estimation of potassium. A. J. W.

**Estimation of Zinc in Zinc Dust.** L. A. WILSON (*Eng. and Min. J.*, 1918, **106**, 334—336).—A sample of zinc dust with ferrous sulphate and a piece of platinum foil are placed in a small conical flask connected through a three-way tap with a measuring tube. The whole system is then filled with liquid saturated with hydrogen at the temperature of experiment, the flask and connecting tube containing water and the measuring tube 10% sulphuric acid. The addition of sulphuric acid through a separating funnel causes evolution of hydrogen, and if any fine particles of zinc are carried over, solution is completed by the acid in the measuring tube. Finally, water is run through the separating funnel to force the hydrogen into the measuring tube, and, after levelling, the volume is read off and corrected. C. A. K.

**Microchemical Reaction for Manganese.** J. B. MENKE (*Chem. Weekblad*, 1918, **15**, 868—869).—A drop of ammonia containing cyanuric acid gives with manganese sulphate a precipitate of manganous hydroxide. After a few minutes, or immediately on boiling, colourless, unstable needles of high polarising power separate from the mixture. A. J. W.

**Rapid Method for the Estimation of Iron in small Quantities of Blood.** LOUIS BERMAN (*J. Biol. Chem.*, 1918, **35**, 231—236).—The iron held in combination in the blood is liberated by the action of concentrated hydrobromic acid, whilst the organic matter is destroyed by potassium permanganate and the iron simultaneously oxidised to the ferric condition. The resulting solution is mixed with a solution of ammonium thiocyanate in water and acetone, and the colour compared with that of a standard iron solution similarly treated. The ordinary ashing process is

thus eliminated, and the estimation requires only 0·040 c.c. of blood, and may be completed in ten to fifteen minutes.
H. W. B.

**Estimation of Chromium in the Presence of Iron.** K. Schorlemmer (*Collegium*, 1918, 145—149).—Iron salts must be removed previous to the estimation of chromium by means of thiosulphate. The solution is treated with hydrogen peroxide, heated, then cooled, and reoxidised by the addition of a further quantity of hydrogen peroxide; the ferric hydroxide is collected, dissolved in acid, twice oxidised with hydrogen peroxide, again collected, and the filtrate added to the first filtrate. The chromium is then estimated in the solution. A further treatment of the ferric hydroxide with hydrogen peroxide may be necessary if much iron is present.
W. P. S.

**Analysis of Molybdenum Ores containing Copper.** W. Hoepfner and O. Binder (*Chem. Zeit.*, 1918, **42**, 315).—Small quantities of copper in an ammoniacal solution of molybdic acid cannot be precipitated by the addition of ammonium sulphide, since copper is soluble to the extent of 0·015 gram (or more) per 100 c.c. of the sulphide solution. To effect the separation of the copper, the ammoniacal solution should be acidified with sulphuric acid and the copper deposited electrolytically after the addition of nitric acid.
W. P. S.

**Ilsemannite.** H. F. Tancy (*Met. and Chem. Eng.*, 1918, (186).—Ilsemannite is a blue compound of molybdenum soluble in water to which the formula $MoO_2,4MoO_3,6H_2O$ is usually given. The molybdenum, occurring as $MoO_2$, may be determined by extracting the ore with hot water, adding to the extract 25% by volume of hydrochloric acid and its own bulk of ether. The mixture is shaken and the layers separated, the aqueous layer being again treated with ether and the ethereal solutions combined. This ether extract is washed ten times with 10 c.c. of hydrochloric acid diluted with 25 c.c. of water to remove iron. The blue compound is titrated with *N*/100-permanganate in a sulphuric acid solution. The total molybdenum present is determined by fuming the solution with strong sulphuric acid, diluting it with water, and adding sodium hydroxide. A precipitate of the hydroxides of manganese and iron is filtered off, the filtrate acidified with 2·5% sulphuric acid, and passed while hot through a Jones reductor. F. C. Th.

**Estimation of Tungsten and Vanadium in the Presence of Titanium.** G. Fenner (*Chem. Zeit.*, 1918, **42**, 403).—To separate tungsten from titanium in a mineral, the latter is fused with sodium peroxide, cooled, the fused mass boiled for a few minutes with water, and the solution then filtered; the titanium remains insoluble, whilst the tungsten passes completely into the filtrate. This method cannot be used for the separation of vanadium from titanium, since the greater part, if not all, of the vanadium remains insoluble. In this case, the mineral, after silica has been removed by treatment with hydrofluoric acid and sulphuric acid, is fused with sodium pyrosulphate, the fused mass dissolved in dilute sulphuric acid, the solution filtered, and the filtrate treated with hydrogen peroxide until a distinct coloration has developed, an excess of the peroxide being avoided. Ammonium fluoride is then added; this destroys the yellow colour of the titanium compound, but does not affect the reddish-brown colour of the vanadium compound. After the yellow colour due to iron salts has been removed by the addition of phosphoric acid, the vanadium is estimated colorimetrically, using a standard prepared under the same conditions and as far as possible with the same quantities of reagents. W. P. S.

**Quantitative Analysis of Vanadium Compounds with the Aid of Carbon Tetrachloride.** Paul Jannasch and Henry E. Harwood (*J. pr. Chem.*, 1918, [ii], **97**, 93—137).—The application of carbon tetrachloride as a reagent for quantitative analysis (Jannasch and others, A., 1913, ii, 876; 1910, ii, 1076; 1909, ii, 728, 767; 1908, ii, 685; 1907, ii, 864) is extended by its use for the estimation of vanadium in its compounds. The vanadium compound in a silica boat enclosed in a silica tube is heated in a current of carbon dioxide and carbon tetrachloride vapour, the resulting vanadium chlorides being collected by passage into dilute nitric acid and water successively. The vanadic acid solution thus obtained is reduced to vanadyl sulphate, the amount of which can then be estimated volumetrically with potassium permanganate. [See also *J. Soc. Chem. Ind.*, October.] D. F. T.

**Application of Rapidly Rotating Metallic Reductors in the Estimation of Vanadic Acid.** F. A. Gooch and W. Scott (*Amer. J. Sci.*, 1918, [iv], **46**, 427—436).—The reduction of vanadic acid in the presence of dilute sulphuric acid may be effected quickly by the aid of rapidly rotating anodes of silver or copper in an electrolytic cell or by a rapidly rotating cylinder of zinc, over-reduction being corrected by the addition of silver sulphate, which automatically forms vanadium tetroxide. The completion of the reduction is indicated by the appearance of precipitated silver in the solution. The reduced liquid is boiled to coagulate the silver, filtered, diluted, again heated to boiling, and titrated with potassium permanganate. The correction applied is variable when an electrode of commercial copper is used, but an electrode of silver plated with copper from a solution of copper sulphate, free from iron, is satisfactory. When zinc is the reducing agent, the results are comparable only if the volume and temperature of the solution, the relative size of the zinc cylinder, and its rate of rotation are kept constant. A. B. S.

**Electroanalysis of Bismuth without Platinum Electrodes.** Pelayo Poch (*Anal. Fis. Quim.*, 1918, **16**, 520—533).—An account of experiments on the estimation of bismuth in solution in nitric, tartaric, sulphuric, and acetic acids, and in ammoniacal solution. In each case, the estimation was carried out with platinum electrodes, with a platinum anode and a copper cathode, with a platinum cathode and an iron or graphite anode, and with a copper cathode and an iron or graphite anode. A. J. W.

**The Copper Method for Estimating Glycerol.** F. L. Weiss (*Chem. Weekblad*, 1918, **15**, 862—868).—There is no compound of copper and glycerol of constant composition, but the proportion of copper depends on four factors: (1) The proportion of glycerol in the solution, the amount of copper increasing with the glycerol. (2) Any rise of temperature, which lowers the proportion of copper, especially in very dilute solutions. (3) The degree of dilution of the liquid. (4) The concentration of the free alkali. A. J. W.

**The Estimation of Phenol in "Cresylic Acid."** J. J. Fox and M. F. Barker (*J. Soc. Chem. Ind.*, 1918, **37**, 265—268T).—For the estimation of phenol in commercial 'cresylic acid' by the method previously described (A., 1917, ii, 513), a number of additional details are given. In place of ether, benzene may be used for getting rid of tar oils and bases, but since benzene is obstinately retained by the solution of the tar acids in sodium hydroxide solution, this solution must be heated sufficiently strongly before acidification to expel all the benzene. Benzene may also be used in place of ether to extract the tar acids after acidification, the washing and drying being carried out as described before. The neutral oils and bases may also be removed by dissolving the tar acids in sodium hydroxide solution and steam distilling, but care must be taken that the sodium hydroxide is in sufficient excess to prevent any tar acids, particularly *o*-cresol, being carried over with the steam.

A short method has been devised for determining whether a sample of 'cresylic acid' contains more than about 5% of phenol. The dried tar acids are fractionally distilled in the standard apparatus described, and the fraction distilling up to 210° is collected and redistilled. The portion boiling up to 202° is collected, and if this is less than 5% the sample is satisfactory. If it is more than 5%, it is again distilled, and the fraction boiling up to 195° is collected and the phenol estimated by a specific gravity determination.

A bibliography of papers dealing with phenol and cresol estimations and separations is appended. E. H. R.

**Chemical Diagnosis of Picric Jaundice. Possible Simulation of Bile Pigments in the Urine.** Domenico Ganassini (*Boll. chim. farm.*, 1918, **57**, 161—167).—The author describes methods of detecting the simulated catarrhal jaundice caused by the ingestion of picric acid by individuals (in Italy) wishing to escape military service, these methods being modifications of Le Mithouard's reaction (*Presse médical.*, 1916, No. 27, 475), the triaminophenol reaction (compare Rodillon, A., 1915, ii, 805), and Derrien's diazo-reaction (*Presse médical.*, 1915, No. 35, 285) for the detection of picric acid derivatives in the urine. It is pointed out that Le Mithouard's reaction is given also by Martius-yellow and by naphthol-yellow S, the latter being a harmless colour allowable in food products; these colouring matters do not, however, respond to the other two reactions mentioned.

Only in exceptional cases of picric jaundice may the picramic acid in the urine be accompanied by bile pigments, this being so especially when large doses of picric acid have been ingested. It is found that the possibility exists of simulating the presence of bile pigments in a urine which does not contain them, for instance, by addition of either a pinch of antipyrine mixed with a trace of alkali nitrate or a very small quantity of Congo-red; a method is given for detecting this fraud, which may be practised to render the jaundice more certain. T. H. P.

**Identification and Estimation of Potassium Guaiacolsulphonate.** SAMUEL PALKIN (*J. Ind. Eng. Chem.*, 1918, **10**, 610—612).—Potassium guaiacolsulphonate as used in medicine is usually mixed with gums, resins, alkaloids, etc. To detect the presence of the sulphonate, the sample is treated with dilute hydrochloric acid, filtered, and a portion of the filtrate tested for sulphates before and after oxidation with sodium peroxide (in the acid solution); any increase in the quantity of sulphate after oxidation indicates the presence of a sulphonate. Another portion of the filtrate is rendered alkaline and treated with a drop of diazotised *p*-nitroaniline; a deep red coloration, changing to yellow when acidified, denotes the presence of guaiacolsulphonate. In the absence of much organic matter, a portion of the sample may be distilled with the addition of phosphoric acid and sodium chloride; the filtrate gives a green coloration with ferric chloride, and, when rendered ammoniacal, reduces silver nitrate. Potassium guaiacolsulphonate may be estimated from the amount of sulphuric acid formed when it is oxidised by repeated evaporation with bromine and nitric acid. W. P. S.

**Estimation of Acetic Acid by Distillation with Phosphoric Acid.** W. FAITOUTE MUNN (*J. Ind. Eng. Chem.*, 1910, **10**, 550—552).—For the estimation of acetic acid in calcium acetate residues, etc., the sample is distilled with the addition of dilute phosphoric acid, and the distillate is collected in a receiver containing an excess of standardised barium hydroxide solution. A current of air free from carbon dioxide is drawn through the apparatus during the distillation, and dilute phosphoric acid is admitted to the distillation flask at the same rate as that at which the liquid distils. When the distillation is completed (this requires about ninety minutes), the contents of the receiver are titrated with *N*/10-hydrochloric acid, using phenolphthalein as indicator; this gives the excess of barium hydroxide. If any barium carbonate has formed, due to the presence of carbonates in the sample, the barium carbonate is dissolved by adding *N*/1-hydrochloric acid in slight excess and then titrating the excess with *N*/1-sodium hydroxide solution, using methyl-orange as an external indicator. Allowance is made for the quantity of carbonate thus found. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**The Detection of *d*-Glycuronic Acid and other Acids with similar Behaviour by the Naphtharesorcinol Reaction.** A. W. VAN DER HAAR (*Biochem. Zeitsch.*, 1918, **88**, 205—212).—An application of Neuberg and Saneyoshi's modification of Tollens's reaction, as applied to plant products. The substance is first hydrolysed with 5% sulphuric acid, the mixture is then neutralised with barium hydroxide, and concentrated after filtration. Lead acetate is then added, and, after filtration, basic lead acetate; the glycuronate is contained in the precipitate thus produced, and this is then heated with 10 c.c. of 10% hydrochloric acid and 100 mg. of naphtharesorcinol for one minute. After cooling to 50°, benzene is added, and if glycuronic acid is present, this on shaking takes up a violet pigment, which gives a characteristic *D*-band of the spectrum. S. B. S.

**Estimation of Phthalic Anhydride in Crude Phthalic Acid.** CHARLES R. DOWNS and CHARLES G. STUPP (*J. Ind. Eng. Chem.*, 1918, **10**, 596—598).—The sample is volatilised from a small glass capsule, and the volatilised phthalic anhydride collected in a tube containing cotton wool, the lower end of this tube being inserted in the neck of the capsule. The capsule is heated at 220°, and a current of air drawn through the apparatus during the operation. The cotton wool is then removed from the tube, boiled with an excess of standard sodium hydroxide solution for thirty minutes, the solution then treated with an excess of standard acid, again boiled, and titrated, using phenolphthalein as indicator. Each c.c. of *N*/10-sodium hydroxide solution is equivalent to 0·0074 gram of phthalic anhydride. The non-volatile residue remaining in the capsule may also be weighed. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**Dropping-point Apparatus for the Examination of Fats, Waxes, and Bitumens.** F. DUPRÉ (*Chem. Zeit.*, 1918, **42**, 398. Compare Ubbelohde, A., 1905, ii, 658).—The substance to be tested is placed in a small metal nipple which is attached to the bulb of a thermometer so that the lower part of the bulb is immediately above the surface of the substance. The thermometer is suspended in a test-tube, which is immersed in a heating-bath heated to about 20° below the probable dropping point of the substance, and the temperature is raised at the rate of 1° per minute until a drop of the melted substance falls from the nipple.

W. P. S.

**Method for Estimating Citral. A Modification of the Hiltner Method.** C. E. Parker and R. S. Hiltner (*J. Ind. Eng. Chem.*, 1918, **10**, 608—610).—Some samples of lemon and orange oils and extracts yield a blue or green coloration when treated with *m*-phenylenediamine hydrochloride, thus limiting the applicability of Hiltner's method, which depends on the formation of a yellow coloration. The addition of oxalic acid, however, inhibits the production of the blue or green coloration, and it is recommended that the reagent be prepared as follows: One gram of *m*-phenylenediamine hydrochloride and 1 gram of crystallised oxalic acid are dissolved separately in 80% alcohol, the solutions are mixed, diluted to 100 c.c. with 80% alcohol, treated with Fuller's earth, and filtered. W. P. S.

**Detection of Acetone.** I. M. Kolthoff (*Pharm. Weekblad*, 1918, **55**, 1021—1029).—Vanillin can replace salicylaldehyde in Frommer's test for acetone (*Berl. Klin. Wochenschr.*, 1902, **42**, 1005) with similar results. The presence of acetaldehyde or formaldehyde is prejudicial. A. J. W.

**Estimation of Acetone.** Allan J. Field (*J. Ind. Eng. Chem.*, 1918, **10**, 552).—Messenger's volumetric method, depending on the formation of iodoform, was found to be untrustworthy; the use of arsenious acid in place of thiosulphate for the titration (compare Vaubel and Scheuer, A., 1905, ii, 291) yielded no advantage. Robineau and Rollin's method as modified by Kebler (*J. Amer. Chem. Soc.*, 1897, **19**, 316) is the most trustworthy for the estimation of acetone; the results are not affected by the presence of alcohol or by differences in the time of shaking.

W. P. S.

**Method for the Separation and Quantitative Estimation of the Lower Alkylamines in the Presence of Ammonia.** F. C. Weber and J. B. Wilson (*J. Biol. Chem.*, 1918, **35**, 385—410).—The *total volatile nitrogen* is first estimated by distillation of the alkaline solution containing ammonia and the amines into 0·05*N*-acid, and titration of the excess of acid with 0·02*N*-alkali, using methyl-red as the indicator.

For the estimation of the *total amines*, a volume of the original solution containing an amount of total volatile nitrogen equivalent to from 40 c.c. to 60 c.c. of 0·05*N*-acid is placed in a 500 c.c. volumetric flask, diluted with water to within 20 c.c. of the mark, and treated with 10 c.c. of an alkaline mixture composed of equal parts of 20% sodium hydroxide and 30% sodium carbonate solutions. After making to the mark, 0·1 gram of yellow oxide of mercury is added for each c.c. of $0{\cdot}1N$-acid equivalent to the total volatile nitrogen. The flask is covered with a black cloth and shaken for one hour. The solution is then filtered through a cotton filter under pressure, and two 200 c.c. portions of the filtrate are distilled into 25 c.c. of $0{\cdot}05N$-acid. The acid neutralised is equivalent to the amines present, from which the total amines may be calculated. The difference between the total volatile nitrogen and the total amines represents the *ammonia* nitrogen.

The distillate containing the total amines is acidified with 0·5 c.c. of concentrated sulphuric acid and evaporated to 35 c.c. It is transferred to a 50 c.c. flask and diluted with water to the mark. The *monoamines* are now estimated in 10 c.c. in the Van Slyke amino-nitrogen apparatus, using the mixing bulb of the large size apparatus and the measuring burette of the micro-apparatus. The remaining 40 c.c. are transferred to a 200 c.c. flask and treated with 20 c.c. of a saturated solution of sodium nitrite and 10 c.c. of glacial acetic acid. The liquid is shaken from time to time to remove as much gas as possible, and, after an hour, a drop of phenolphthalein indicator is added and 30 c.c. of a 20% sodium hydroxide solution. On mixing, the solution should remain acid; if it begins to turn red, a few drops of acetic acid are added. After a few hours, 15 c.c. to 20 c.c. more of the sodium hydroxide solution are added, and it is distilled into 25 c.c. of $0{\cdot}05N$-sulphuric acid. It is titrated back as before with $0{\cdot}02N$-alkali, using methyl-red as indicator. The acid used is equivalent to the *triamines*. The *diamines* may be estimated by difference, or by the following method. To the distillate containing the triamine (and also the diamine in the form of nitrosoamine) 10 c.c. of concentrated hydrochloric acid and a few grams of granulated zinc are added, and when hydrogen is being evolved freely it is placed over a small flame and heated to boiling. The solution is decanted from the remaining zinc, which is washed with three 10 c.c. portions of water. After addition of a drop of phenolphthalein and about 10 grams of sodium hydroxide, the product is distilled into 25 c.c. of $0{\cdot}05N$-acid, and titrated back as before. The acid used is equivalent to the sum of the diamines and triamines present.

The method appears to give accurate results, and may be employed in the analysis of fish products, putrid flesh, bad sausages, biological fluids, etc. H. W. B.

**Evaluation of Hexamethylenetetramine Tablets.** W. O. EMERY and C. D. WRIGHT (*J. Ind. Eng. Chem.*, 1918, **10**, 606—608).—A portion of the sample is boiled under a reflux apparatus with dilute hydrochloric acid, and the solution is then made up to a known volume. An aliquot portion of this solution is treated at 0° with alkaline potassium mercuric iodide solution (a modified Nessler reagent); the formaldehyde is oxidised to a formate, and an equivalent amount of metallic mercury is precipitated. The mixture is then acidified with acetic acid, and an excess of $N/10$-iodine solution added; the iodine combines with the mercury, and the excess of iodine is titrated with thiosulphate solution. [See, further, *J. Soc. Chem. Ind.*, October.]

W. P. S.

**Abnormalities in the Formol Titration Method.** S. L. JODIDI (*J. Amer. Chem. Soc.*, 1918, **40**, 1031—1035).—An explanation is given of the abnormalities which sometimes render untrustworthy Sörensen's formaldehyde titration method of estimating amino-acids, polypeptides, etc The function of the formaldehyde is to convert the basic nitrogen in the molecule into a neutral group, so that the carboxyl group can be accurately titrated; in the case of simple amino-acids, $NH_2 \cdot R \cdot CO_2H$, containing only amino- and carboxyl groups, the reaction is

$$NH_2 \cdot R \cdot CO_2H + CH_2O = CH_2 \colon N \cdot R \cdot CO_2H + H_2O;$$

the group $CH_2 \colon N \cdot$ is neutral, and the resulting monobasic acid contains no groups modifying its acidity. Proline, however, contains an imino-group, and reacts with formaldehyde to give methyleneproline containing the group $\colon N \cdot CH_2 \cdot N \colon$, which is still somewhat basic, with the result that the formaldehyde method gives too low results. The same holds for hydroxyproline. The product from formaldehyde and histidine also contains the group $\colon N \cdot CH_2 \cdot N \colon$, and the estimation is therefore low, but the result is better than in the case of proline, probably owing to the acidic nature of the azole nucleus. Tryptophan has not yet been estimated by Sörensen's method, but in view of the presence of an imino-group, it seems safe to predict that the result will be low. In the case of lysine, the method gives low results, although an accurate result would be expected, since the molecule contains, apart from the two amino-groups, no groups which could affect the carboxyl group; the discrepancy is attributed to the distance of the $\omega$-amino-group from the carboxyl group.

C. S.

**Analysis of Calcium Cyanamide containing much Dicyanodiamide and Urea.** E. HENE and A. VAN HAAREN (*Zeitsch. angew. Chem.*, 1918, **31**, 129—131).—A solution of the cyanamide, dicyanodiamide, and urea is prepared in the usual way, and an aliquot portion, containing about 0·2 gram of nitrogen, is diluted to 200 c.c. and treated with 20 c.c. of 10% silver nitrate solution and 30 c.c. of 10% potassium hydroxide solution; the precipitate, which contains all the cyanamide and dicyanodiamide and some of the urea, is washed, mixed with 150 c.c. of water, dissolved in the minimum quantity of nitric acid, diluted to 200 c.c., and 100 c.c. of this solution are treated with 2 c.c. of silver nitrate solution and 15 c.c. of potassium hydroxide solution. The precipitate, which now contains all the cyanamide and dicyanodiamide, is collected and the nitrogen in it determined by Kjeldahl's method. In another portion of the original solution, the cyanamide is precipitated by means of silver nitrate and ammonia, and the nitrogen determined in the precipitate; the difference between this and the first nitrogen determination gives the dicyanodiamide nitrogen.

The urea nitrogen is found from the difference between the sum of the cyanide and dicyanodiamide nitrogen and the total nitrogen in the sample. W. P. S.

**[Estimation of] Creatinine in Blood.** I. CHERTKOV (*Rev. méd. suisse romande*, 1917, **37**, 748; from *Physiol. Abstr.*, 1918, **3**, 247).—Protein is precipitated by trichloroacetic acid; to the filtrate, sodium hydroxide and picric acid are added, and the creatinine is estimated colorimetrically. S. B. S.

**Estimation of Theobromine.** W. O. EMERY and G. C. SPENCER (*J. Ind. Eng. Chem.*, 1918, **10**, 605—606. Compare A., 1914, ii, 825).—A method for the estimation of theobromine, either alone or mixed with sodium acetate and sodium salicylate, depends on the formation of its periodide, $C_7H_8O_2N_4,HI,I_4$. A quantity of 0·1 gram of the sample (with an equivalent quantity of sodium acetate in the case of theobromine alone) is dissolved in 2 c.c. of glacial acetic acid, 5 c.c. of hot water are added, and the solution is transferred to a 100 c.c. flask containing 50 c.c. of *N*/10-iodine solution; 20 c.c. of saturated sodium chloride solution and 2 c.c. of concentrated hydrochloric acid are then added, and, after about eighteen hours, the mixture is diluted to 100 c.c., filtered, and the excess of iodine titrated in an aliquot portion of the filtrate. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**Method for making Electrometric Titrations of Solutions containing Protein.** JOHN C. BAKER and LUCIUS L. VAN SLYKE (*J. Biol. Chem.*, 1918, **35**, 137—145).—The apparatus consists of a wide-mouthed bottle, holding about 400 c.c., provided with a cork stopper containing perforations through which the several parts or connexions pass into the bottle. The hydrogen electrode, made of platinum foil, is suspended in a special manner inside the bell-shaped end of the tube carrying hydrogen, and is so arranged that it can be lowered into or drawn out of the solution titrated. Other parts are (*a*) a glass tube admitting the titration reagent from a burette into the solution titrated, (*b*) special stirring apparatus, (*c*) a tube for introducing additional reagents, (*d*) a tube containing potassium chloride, and, in addition, other pieces of apparatus required to measure the hydrogen-ion concentration.

In operating, the solution under examination is placed in the bottle, and hydrogen passed in, the electrode being above the solution. The stirrer being in motion, the electrode is lowered into the solution, electric connexions are made, equilibrium is established, and then the titration reagent run in. Readings of the *E.M.F.* are made once a minute until constant, and titration is then continued. The apparatus is designed to prevent local chemical action at the point where the reagent enters the solution under titration. H. W. B.

# General and Physical Chemistry.

**Spectrochemistry and Determination of the Constitution of Tautomeric Compounds.** K. von Auwers (*Annalen*, 1918, **415**, 169—232).—Brühl showed more than thirty years ago that molecular refraction and dispersion can be utilised to differentiate between enolic and keto-modifications, but the determination in recent times of the composition of keto-enol mixtures by chemical means has frequently led to results which are quite opposed to Brühl's views. The author has undertaken a series of researches, of which this is the first, to ascertain how far spectrochemistry in its present state can be applied to investigations of desmotropic compounds.

With the difference in structure represented by the scheme $\cdot CO\cdot CHR\cdot \rightleftharpoons \cdot C(OH):CR\cdot$ correspond constant differences in the molecular refraction and dispersion of such magnitudes that a trustworthy decision between the two structures can be made when only homogeneous substances are in question; also the percentage composition of mixtures of simple enols and ketones, for example, a simple unsaturated alcohol and the isomeric aldehyde or ketone, can be ascertained with satisfactory accuracy by the refractometric method, especially if the specific refraction and dispersion are employed instead of the molecular magnitudes. Errors arise, however, and false conclusions may be drawn when certain groups are present in the molecule. For example, in β-diketones, β-ketonic acids, etc., occur the systems $\cdot CO\cdot CHR\cdot COR'$ and

$$OH\cdot C:CR\cdot CR':O.$$

The former is spectrochemically normal, but the latter, containing a conjugate system of linkings, exhibits an abnormal increase of the refraction, and still more so of the dispersion. Almost the only possible way of overcoming this difficulty is the calculation of the magnitude of the exaltations by means of known regularities. Eisenlohr and Auwers (A., 1910, ii, 365; 1911, ii, 781) have shown that the magnitudes of the specific exaltations of the refraction and dispersion remain practically constant in compounds containing the same conjugate system, so that 'normal values' of the specific exaltations can be recorded. Unfortunately, this regularity is not equally sharp in all classes of substances, possibly on account of experimental error or of lack of purity of the compounds examined. It is necessary, therefore, to determine more accurately than hitherto the normal values of the specific exaltations for the conjugate systems $\cdot CH:CH\cdot CR:O$ and $\cdot CH:CH\cdot C(OR):O$, and to ascertain the influence of disturbing substituents on these values. By means of the numbers so obtained, the theoretical values of the molecular refraction and dispersion of the enols could be calculated, and thus the foundations laid for a more trustworthy determination of the equilibrium proportions of enolic and keto-modifications by means of the optical constants. The author then discusses the values obtained for series of hydroxymethylene compounds and their ethers and esters, and draws the conclusion that a trustworthy calculation of the real molecular refraction and dispersion of enols is possible at the present time only in a few cases in which specially favourable comparison material is available. The following substances have been examined. The percentages are calculated from the spectrochemical data, and the figures in brackets are the percentages found by Meyer's bromine method. Ethyl diacetoacetate, percentage of keto-enol 100 (90—100); acetylacetone, enol 69% (76); methylacetylacetone, keto-enol 38% and 31% in two different preparations (31); ethylacetylacetone, keto-enol about 27%; ethyl acetylmalonate, enol 70% (64); methyl benzoylacetate, enol 25% (16·7); ethyl benzoylacetate, enol 29% (29); ethyl α-benzoylbutyrate, enol at most a few units per cent.; methylbenzoylacetone, enol 22% (6).

The spectrochemical constants (density and refractive indices for the α-, *D*-, β-, and γ-lines) have been determined of the following hydroxymethylene compounds and their ethyl ethers and acetates; γ-keto-β-methyl-$\Delta^{\alpha}$-penten-α-ol; hydroxymethylenepinacolin (*ethyl* ether, b. p. 103—104°/16 mm.; *acetate*, rhombohedral plates, m. p. 44—45°, b. p. 118—118·5°/16 mm.); 2-hydroxymethylene*cyclo*hexanone (*ethyl* ether, b. p. 128·2—128·4°/16 mm.; *acetate*, b. p. 142—143°/14 mm.); 2-hydroxymethylenementhone; ethyl β-acetoxyacrylate; ethyl β-hydroxy-α-methylacrylate; ethyl hydroxymethyleneacetoacetate; ethyl hydroxymethylenemalonate. The constants are also given for the following diketones and ketonic esters: acetylacetone (and the O-methyl and -ethyl ethers); methylacetylacetone; dimethylacetylacetone; ethylacetylacetone; methylbenzoylacetone (and the O-methyl ether); β-methoxy-β-amylacrylic acid and its methyl ester; ethyl β-ethoxy-β-amylacrylate; ethyl O-acetylacetoacetate; ethyl diacetoacetate; methyl benzoylacetate and the ethyl ester; ethyl ethylbenzoylacetate. C. S.

**Atomic Refraction and Atomic Dispersion of Quadrivalent Lead, Deduced from the Saturated Lead Tetra-alkyls.** GERHARD GRÜTTNER and ERICH KRAUSE (*Annalen*, 1918, **415**, 338—362).—Hitherto, the atomic refraction of quadrivalent lead, 17·87 for the red hydrogen line ($n^2$ formula), has been deduced from only one compound, lead tetra-ethyl. Since it is known that the atomic refraction of silicon, deduced from the silanes, varies between 7·0 and 8·0, it is very desirable that the value for lead should be recalculated, and for this purpose the numerous lead tetra-alkyls prepared by the authors in 1916 and 1917 are well suited, since they are colourless, stable liquids. The values of the atomic refraction and dispersion of quadrivalent lead depend on the number of carbon atoms in the molecule, and increase from the $C_4$ to about the $C_{12}$ compounds. The values calculated from the simple, completely symmetrical lead tetra-alkyls ($PbR_4$) increase regularly with the molecular weight. The authors are decidedly of opinion that there are no constant values. The atomic refraction ($H_\alpha$ line) increases from 17·07 for the $C_4$ compound to 18·16 for the $C_{11}$ compounds, and the atomic dispersions increase from 1·43 to 1·75 ($H_\gamma$—$H_\alpha$), and from 0·87 to 1·05 ($H_\beta$—$H_\alpha$).

Certain regularities in the b. p.'s, densities, and refractions and dispersions of lead alkyls and silicon alkyls are recorded. C. S.

**Atomic Number and Frequency Differences in Spectral Series.** HERBERT BELL (*Phil. Mag.*, 1918, [vi], **36**, 337—347).—It has been previously shown by Rydberg and by Kayser and Runge that for elements in the same periodic group the wave-number differences between the components of doublet and triplet series are approximately proportional to the squares of the atomic weights. This relation has been further examined, the atomic weights being replaced by the atomic numbers.

By plotting the square root of the wave-number difference against the atomic number, straight lines are obtained corresponding with the equation $\sqrt{\nu}=m(N-N_0)$, in which $N$ is the atomic number of the element and $m$ and $N_0$ are constants. In the first group, the elements lithium, sodium, potassium, rubidium, and cæsium fall on one straight line, for which $m=0·4447$ and $N_0=1·875$, whilst potassium, copper, silver, and gold fall on a second straight line, for which $m=0·8117$ and $N_0=9·619$. There is thus a twofold collinearity in the first group of the periodic table, and this feature is again met with in the second group.

The linear relation between the square root of wave-number differences and atomic numbers has also been found to hold for the members of other groups in the periodic arrangement.

The logarithmic relation $\log\nu=p\log N+q$, which was suggested by Runge and Precht (A., 1903, ii, 346), does not seem to be in better agreement with the facts than the equation $\sqrt{\nu}=m(N-N_0)$. H. M. D.

**Photographic Record of the $K$-Spectra of Platinum and Iridium.** J. E. LILIENFELD and H. SEEMANN (*Physikal. Zeitsch.*, 1918, **19**, 269—271).—The $K$-spectra of platinum and iridium have been examined with the aid of a new type of spectrograph. The intensity distribution in the spectra and the effect of the interposition of a layer of aluminium, as determined by photometric observations, are shown in the form of curves. The photographs obtained show the existence of rays of shorter wave-length than any which have been previously described. H. M. D.

**Spectrum of Cadmium in the Inactive Gases.** J. N. COLLIE and H. E. WATSON (*Proc. Roy. Soc.*, 1918, [*A*], **95**, 115—120).—Making use of tubes fitted with a cadmium cathode and an aluminium anode, and filled with one of the gases helium, argon, neon, or xenon, the authors have observed certain peculiarities in the spectrum of cadmium. The cadmium lines 6438, 5379, 5338, 5086, 4800, 4678, and 4416 were generally seen, but the intensity of the lines varied with the pressure and current. Thus with helium at a pressure of 40 mm., four of the cadmium lines were visible, and with neon at 60 mm. pressure, two were visible. In many cases, the lines 5379 and 5338 were entirely absent and the individual lines varied considerably with the gas employed. In the case of the lines 5379 and 5338, it was found that with helium at 40 mm. they were scarcely visible, whilst at 5 mm. they were the brightest lines of the spectrum; in argon they only became visible at 2·5 mm., whilst in xenon these two and 4678 were the only lines visible when a weak current was used. Tables of the intensities of the lines in helium at various pressures are given for the current values 5 and 0·5 amperes. The line 5086 behaved in an unusual manner, in that whilst the experimental conditions were constant, it suddenly flared up to an intensity equal to that of the brightest of the other lines and then suddenly vanished. In the case of argon, the lines 6438, 5086, 4800, and 4678 were very bright at 21 mm. pressure. At 3 mm. pressure, only 5086 was to be seen, and 5379 and 5338 did not appear until the pressure was reduced to 2·5 mm. In krypton, the results were indefinite; the same applies to xenon. The heating effect of the cathode is progressive, being least with helium and greatest with xenon. J. F. S.

**Origin of the Line Spectrum Emitted by Iron Vapour in an Electric Tube Resistance Furnace at Temperatures above 2500°.** G. A. HEMSALECH (*Phil. Mag.*, 1918, [vi], **36**, 281—296. Compare this vol., ii, 341).—Further observations on the furnace spectrum of iron at high temperatures are described, all of which point to the conclusion that this spectrum is not a purely thermal effect, but is due to the passage of a current through the vapour of the metal. At 2700°, the furnace spectrum is entirely different from the flame spectrum at the same temperature and approaches in character the arc spectrum of the element. Direct evidence has been obtained that a current will readily pass through the vapour in a tube furnace. The line spectrum does not disappear immediately when the heating current is cut off, but is exhibited for some time afterwards, the lines being extinguished gradually. The spectrum emitted after the current is broken does not correspond with the temperature of the cooling vapour. Attempts to obtain a line spectrum under conditions in which electrical action was excluded by the use of a furnace of special design gave a negative result.

The fact that the vapours of copper, silver, and zinc give no line spectrum when subjected to thermo-electric action in the electric tube resistance furnace at 2700° is supposed to be due to the small conductivity of these vapours as compared with that of the vapours of iron, cobalt, and nickel, all of which readily give a line spectrum under the same furnace conditions.

The methods of excitation which give rise to spectral emission in flames, furnace, arc, and spark are severally distinguished and grouped as (*a*) thermal, (*b*) thermo-chemical, (*c*) chemical, (*d*) thermo-electrical, (*e*) electrical. The observations on iron vapour show that the line spectrum cannot be produced by thermal excitation alone. H. M. D.

**Ionisation and Spectral Emission of Different Elements in the Positive Column.** O. HARDTKE (*Ann. Physik*, 1918, [iv], **56**, 383—387).—According to Stark's investigations, the emission of characteristic spectra is associated with positively charged ions. In consequence of differences in the ionising potentials, it is to be expected that when glow discharge takes place through a tube containing several gases, the positive column will show marked differences in the spectral emission at various points. Experiments made with a tube containing mercury, nitrogen, and argon have actually shown a distribution of the spectra of these elements which are in the order to be expected from a consideration of their ionising potentials. In proceeding from the cathode towards the anode end of the positive column, the order in which the characteristic spectra make their appearance is mercury, nitrogen, argon; this is also the order of the positions of maximum intensity of comparable lines. Of the three elements, mercury has the lowest ionisation potential and argon the highest. The distribution of the spectral emission along the positive column is thus found to be dependent on the ionising potentials of the elements concerned. H. M. D.

**Binuclear Quinones. Chemical Action of Light.** HANS MEYER and ALFRED ECKERT (*Monatsh.*, 1918, **39**, 241—251).—As has already been demonstrated (Meyer and Hofmann, A., 1916, i, 641), dihydroanthracene, when heated, readily decomposes into anthracene and hydrogen, and it is therefore to be expected (Meyer and Hofmann, this vol., i, 383) that the same dissociation should occur under the influence of light. Contrary to the statement of Orndorff and Cameron (A., 1896, i, 176), this substance does undergo chemical alteration when exposed to light from the sun or electric arc, the products being hydrogen and para-anthracene, the latter being formed by the immediate polymerisation of the "nascent" anthracene, which is the primary product; in the presence of substances capable of reacting with the "nascent" anthracene, other products may be obtained. The action of light on anthracene probably also first gives rise to "nascent" anthracene in which the diagonal valency becomes resolved into two free valencies; by these the formation of para-anthracene becomes possible; if oxygen is present, the products are anthraquinone and dihydrodianthrone (compare Luther and Weigert, A., 1905, ii, 785), the latter being formed by the further action of light on anthranol, which represents an intermediate stage of the change. It is already known that solutions of benzoquinone and thymoquinone in ethyl alcohol when subjected to light give rise to acetaldehyde and the corresponding quinol. With anthraquinone, however, the quinol derivative is unstable, and in contact with air regenerates anthraquinone; it is therefore possible to use anthraquinone as a catalyst for the oxidation of ethyl alcohol to acetaldehyde in light, the only other product being a small quantity of an unidentified substance which gives a brown solution in aqueous potassium hydroxide. In a similar manner, *iso*propyl alcohol can be oxidised to acetone, but methyl alcohol is very stable and is recovered completely unchanged, together with the anthraquinone. This relative stability of methyl alcohol accords well with the earlier result of Meyer and Hofmann (*loc. cit.*), and may account for the preponderance of methyl derivatives amongst the naturally occurring alkyl compounds. 9:10-Dichloro- and 9:10-dibromoanthracene are unaffected by light, but 10-bromoanthracene in alcoholic solution gradually gives rise to anthraquinone and bromide ions, together with a temporary small deposit of para-anthracene. If dihydroanthracene in acetic anhydride solution is submitted to the action of light, the first deposit of para-anthracene may disappear on prolonged treatment, probably by further oxidation to anthraquinone; anthranyl acetate is obtained as a by-product, its formation supplying an explanation of the origin of dihydrodianthrone in the action of light and air on anthracene in alcoholic solution. Solutions of anthracene in acetic acid, chloroform, and methyl sulphate, when illuminated, give the same products, namely, para-anthracene, anthraquinone, and dihydrodianthrone; it was hoped with the aid of methyl sulphate to isolate anthraquinol in the form of its dimethyl ether, but unfortunately this compound is sensitive to light, and in acetic acid solution is rapidly converted into anthraquinone. D. F. T.

**The Wave-length of the Hard γ-Rays of Radium.** K. W. Fritz Kohlrausch (*Physikal. Zeitsch.*, 1918, **19**, 345—349).—The wave-length of the very penetrating γ-rays emitted by radium-*B* and radium-*C* is discussed with reference to the absorption of the rays in different elements. H. M. D.

**The Electrical Conductivity of Salt Vapours.** Gerhard C. Schmidt (*Ann. Physik*, 1918, [iv], **56**, 341—362. Compare A., 1911, ii, 788; 1913, ii, 747).—Further attempts to obtain reproducible data for the electrical conducting power of salt vapours have given negative results, although various forms of apparatus have been tried with this object in view. The frequently observed fact that the conductivity first increases and then decreases has been traced on the one hand to the slow diffusion of the vapour, and on the other to the caking of the fused salt at the surface, resulting in a reduced rate of vaporisation. The velocities of the positive and negative ions have been determined in the case of cadmium chloride, bromide, and iodide, and of zinc bromide and iodide. Although the results for these different salts are not comparable with one another, they show that the mobility of the negative ions is in all cases greater than that of the positive ions. The ionic mobilities are of the same order of magnitude as those found by previous investigators for the ions produced in the oxidation of phosphorus and for the ions in flame gases at a considerable distance from the flame. The mobility increases with rise of temperature and depends on the average life of the ion in the sense that the mobility is greater the shorter the average life of the ion.

H. M. D.

**New Method for the Determination of Conductivity.** EDGAR NEWBERY (T., 1918, **113**, 701—707).—Kohlrausch's method for the determination of the electrical conductivity of solutions is criticised, and a method is described which utilises direct current and completely eliminates the effect of polarisation at the electrodes. This method is a simple modification of the method used in the measurement of the resistance of a metallic conductor by observing the fall of potential along it during the passage of a known current. The values obtained for the conductivity of *N*-solutions of potassium chloride and sulphuric acid at 25° are respectively 0·3% greater and 3·6% less than the values recorded by Kohlrausch. In the case of *N*-silver nitrate, the two values are very nearly equal.

H. M. D.

**Electrical Conductance of Aqueous Phthalate Solutions.** HARRISON E. PATTEN, ALFRED J. JOHNSON, and GERALD H. MAINS (*J. Amer. Chem. Soc.*, 1918, **40**, 1156—1162).—In reference to the application of potassium hydrogen phthalate as a standard in acidimetry and hydrogen-ion concentration measurements, the authors have measured the conductivity of its aqueous solutions at 25°. The molecular conductivity (corrected for the conductivity of the solvent) was found to increase from 76·9 at $v=5$ to 153·0 at $v=10,000$. Hydrogen-ion concentration measurements gave $c_H=1·29\times10^{-4}$ at $v=5$ and $c_H=1·23\times10^{-4}$ at $v=10$.

The molecular conductivity of normal potassium phthalate is much higher than that of the acid salt, and was found to increase from 184·8 at $v=20$ to 247·0 at $v=5000$.

H. M. D.

**Diamagnetism of Hydrogen and the Value of the Magneton.** A. E. OXLEY (*Proc. Roy. Soc.*, 1918, [*A*], **95**, 58—61).—On the assumption that the molecules of diamagnetic substances contain magnetic elements arranged in such a way that the molecule is self-compensated, so that the application of a magnetic field produces only a diamagnetic effect, it is calculated that the moment of the magneton in the case of hydrogen is equal to $14·7\times10^{-22}$, which agrees closely with the moment for molecules of ferromagnetic and paramagnetic substances ($16·5\times10^{-22}$). If each hydrogen atom contains one magneton, the calculated radius of the electron orbit is about $1\times10^{-8}$ cm.

H. M. D.

**The Coefficients of Magnetisation of Oxygen and of Nitric Oxide, and the Theory of the Magneton.** EDMOND BAUER, PIERRE WEISS, and AUGUSTE PICCARD (*Compt. rend.*, 1918, **167**, 484—487).—The authors have made fresh measurements of the coefficients of magnetisation of oxygen and nitric oxide by three different methods, the values obtained being: for oxygen, $\chi_{20} = 1{\cdot}077 \times 10^{-4} \pm 0{\cdot}003 \times 10^{-4}$, $\sigma_{O_2} = 1{\cdot}587 \times 10^4$; for nitric oxide, $\chi_{20} = 0{\cdot}487 \times 10^{-4} \pm 0{\cdot}0025 \times 10^{-4}$, $\sigma_{NO} = 1{\cdot}033 \times 10^4$. These values are in contradiction with the theory of the magneton, and it is suggested either that oxygen and its compounds are an exception to the general law or that the discrepancies are due to a difference between the kinetic theory and experimental facts. W. G.

**Magnetic Susceptibility of Mixtures of Liquids.** ALPHEUS W. SMITH and ALVA W. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 1218—1224).—Quincke's method has been used in the investigation of the magnetic susceptibility of mixtures of acetone and water, acetic acid and water, acetic acid and benzene, and of acetone and ethyl alcohol. Within the limits of experimental error, the results obtained for the four pairs of substances are in agreement with the requirements of the additive law. It is suggested that the magnetic susceptibility may advantageously be used in the analysis of binary mixtures. H. M. D.

**The Causes of Abnormal Boiling Points.** A. BERTHOUD (*J. Chim. Phys.*, 1918, **16**, 245—278).—A theoretical discussion in which the author shows that de Forcrand's views as to the relationship of the abnormal boiling points of water, hydrofluoric acid, and ammonia to their heats of formation and their molecular dissymmetry (compare this vol., ii, 107) are not in accord with experimental facts. On the other hand, molecular association has the effect of raising the boiling point, but not to the extent often stated. Calculations founded on the additivity of the constants *b* and $\sqrt{a}$ (compare van Laar, A., 1916, ii, 610) indicate that, amongst the substances studied, acetic acid is the only one of which the boiling point and the critical temperature can be explained entirely by association. In cases such as those of water, alcohols, and ammonia, another factor intervenes. The critical pressures of the last-named compounds are also too high, and this cannot be explained on the grounds of molecular association. This other factor, which works with the molecular association in causing high boiling points and critical temperatures in the cases of water and the alcohols, lies in the particularly high value of the constant *a*, independent of the molecular association, in substances containing an –OH group. W. G.

**Freezing Points of Concentrated Solutions and the Free Energy of Solution of Salts.** WORTH H. RODEBUSH (*J Amer. Chem. Soc.*, 1918, **40**, 1204—1213).—Recent improvements in the method of determining the freezing points of dilute solutions (Adams, A., 1915, ii, 222) have been made use of in the investigation of concentrated solutions, the relation between the freezing point and the concentration of various aqueous salt solutions having been followed down to the eutectic temperature. The following data are recorded for the eutectic composition (grams anhydrous salt per 100 of water) and the eutectic temperature: sodium chloride, 30·4, 21·12°; potassium chloride, 24·60, 10·66°; ammonium chloride, 24·50, 15·36°; magnesium chloride, 28·00, 33·50°; calcium chloride, 48·00, 51·0°; potassium bromide, 45·65, 12·60°; sodium nitrate, 62·50, 17·46°; ammonium nitrate, 74·80, 16·67°; ammonium sulphate, 66·40, 18·34°. Temperature measurements were made by the aid of a copper–constantan thermocouple.

The thermodynamic equations required for the calculation of the free energy change which accompanies the formation of solutions of different concentrations are considered and applied to the experimental data for solutions of sodium chloride and potassium chloride.

H. M. D.

**Representation of the Properties of Binary Systems.** G. Masing (*Int. Zeitsch. Metallographie*, 1917, **9**, 82—89; from *Chem. Zentr.*, 1918, i, 800—801).—In the graphic representation of the properties of binary systems in relation to the composition, curves of the most peculiar form can, in certain cases, be obtained by a quite justifiable selection of the independent variables, and from these curves quite unjustifiable conclusions can be drawn. The selection of the variables, therefore, is not immaterial. As composition variable, an additive property such as mass (weight- or atomic-percentage) is suitably selected. The selection of volume percentage, for example, gives complicated curves, on account of volume changes; in electrical conductivity, such a selection would represent the relation between conductivity, composition, and specific volume, instead of the relation between conductivity and composition.

Likewise, the property function ought to be so selected that it is additive for a mechanical mixture. Two principal cases are to be differentiated in the case of alloys. When the property under examination is a purely intensity magnitude, it is independent of the quantity of the phases present, and for a mechanical mixture is represented by a straight line parallel to the concentration axis. In the second case, when the property is a specific magnitude, that is, is calculated on unit quantity of the alloy, this unit must always be the same as that employed in plotting the concentration axis. For example, the specific volume is correctly represented as a function of the weight concentration, but it is incorrect to represent the density as a function of the weight percentage.

The author discusses the representation of density, specific volume, atomic volume, electrical conductivity, and the phenomena of fusion and transition.

C. S.

**The Fluidity and Specific Volume of Binary Liquid Mixtures.** W. Herz (*Zeitsch. anorg. Chem.*, 1918, **104**, 47—52). Compare this vol., ii, 155).—Mixtures of methyl alcohol and ethyl alcohol and of methyl alcohol and propyl alcohol show a linear relationship between fluidity (expressed in *C.G.S.* units) and specific volume. In the case of ethyl alcohol–propyl alcohol mixtures, however, the linear relationship no longer holds, and the curves for mixtures of water with methyl and ethyl alcohols both show a well-marked minimum with approximately 40% alcohol. A number of other mixtures show a linear relationship, for example, trichloroethylene and pentachloroethane, tetrachloroethylene and carbon tetrachloride, tetrachloroethane and carbon tetrachloride, propyl acetate and amyl formate, chlorobenzene and bromobenzene at 12° and 64°, acetic acid and formic acid. E. H. R.

**Surface Deconcentration.** L. BERCZELLER (*Kolloid Zeitsch.*, 1918, **23**, 31—35).—Measurements have been made of the surface tension of aqueous solutions of phenol, valeric acid, thymol, and hæmoglobin in presence of varying quantities of different alcohols, the object being to determine to what extent the depression of the concentration of the solute at the surface of the solution by the alcohol is dependent on the concentration of the latter. The surface tension measurements were made by means of a Traube stalagmometer, the drop-numbers being taken for convenience as a measure of the surface tension. As a measure of the surface deconcentration, the difference, $\Delta$, between the drop-number of the solution containing both alcohol and solute under examination and that of a solution containing alcohol alone is taken.

The influence of the concentration of ethyl, propyl, and *iso*amyl alcohols on aqueous solutions of phenol is expressed by the equation $(\Delta\sqrt[3]{P^2})/\sqrt{D}=\text{const.}$, where $P$ is the concentration of the alcohol and $D$ is proportional to the lowering of the surface tension of water by alcohol of concentration $P$. In the case of methyl alcohol, however, a better constant is obtained if, in the above equation, $D$ is substituted for $\sqrt{D}$. The effect of the four alcohols on aqueous solutions of valeric acid and thymol, respectively, is satisfactorily represented by the original equation, although in the case of thymol at high concentration of alcohol the expression no longer holds. In the case of hæmoglobin, the constancy of the expression is restricted to still smaller ranges of concentration of alcohol. It is noteworthy that for each of the four solutes examined, the constants found for the alcohols, methyl, ethyl, propyl, and *iso*amyl, are always in the same proportion, approximately 5:4:3:1. Further, when the constants found for each alcohol are divided by the factor $D_0$, the lowering of the surface tension of water by the solute examined, constants are obtained which are characteristic for the different alcohols and almost independent of the character of the solute. E. H. R.

**Adsorption by Hide-powder. II.** VÁCLAV KUBELKA (*Kolloid Zeitsch.*, 1918, **23**, 57—68. Compare A., 1916, ii, 297).—Observations on the adsorption of hydrogen chloride from aqueous solutions by hide-powder are described. Over a period of two years, the hide-powder was found to have the same adsorption capacity. From pure aqueous solutions of hydrogen chloride, the quantity of this which is adsorbed by the hide-powder is independent of the concentration of the solution. In presence of considerable quantities of sodium chloride, this relation no longer obtains. The adsorption in these circumstances increases with the concentration of the acid, and the form of the adsorption curve suggests that the phenomenon is of complex character. It seems probable that the first portions of acid which are removed from solution combine with the hide-powder to form a definite chemical compound. This compound appears to contain about 977 grams of hide-powder per gram-molecule of hydrogen chloride. This number agrees fairly closely with those which have been previously obtained for the molecular weight of gelatin. The further removal of hydrogen chloride from solution takes place in agreement with the usual adsorption formula. It thus appears that there are two distinct processes involved in the so-called adsorption of hydrogen chloride by hide-powder. [Compare *J. Soc. Chem. Ind.*, 665A.]

H. M. D.

**The Rate of Capillary Ascension of Liquids.** RICHARD LUCAS (*Kolloid Zeitsch.*, 1918, **23**, 15—22).—From Poiseuille's expression for the rate of flow of liquids in capillary tubes, the author has deduced the expression, for the rate of ascension of a liquid in a capillary tube, $h^2 = \omega/\eta \,.\, r/2 \,.\, \cos d \,.\, t$, where $h$ is the height to which the liquid rises in time $t$, $\omega$ the surface tension, $\eta$ the viscosity, $r$ the radius of the tube, and $d$ the meniscus angle. This formula is identical in form with Ostwald's empirical formula, $h^{1/m} = kt$, if $m$ is made $= 0{\cdot}5$. Experiments have been made on the rate of ascension of a number of liquids in filter-paper, the liquids used being glycerol, aniline, nitrobenzene, benzene, methyl and ethyl alcohols, ether, chloroform, carbon tetrachloride, and carbon disulphide. Three grades of filter-paper were used of widely differing porosity, and in every case the results were satisfactorily expressed by Ostwald's equation, the value of $m$, however, being always less than 0·5 but greater than 0·4. If $k$ is expressed in absolute units, the equation can be written $k\eta/\omega = r/2 \,.\, \cos d \,.\, t =$ const. The value of this constant is independent of the liquid used and is proportional to the mean diameter of the pores of the paper. The values of this constant obtained from the different liquids for each paper agreed satisfactorily, the ratios of the porosities of the three papers used being found to be 1 : 4 : 12·5.

It is to be observed that the formula $h^2 = \omega/\eta \,.\, r/2 \cos \,.\, d \,.\, t$, being an approximation, is only strictly true when the capillary rise is still far from completion, that is, when $h$ is small compared with $h_0$, the maximum rise. The formula cannot therefore be expected to hold for glass capillaries, in which the rate of ascension is very rapid.

E. H. R.

**Theory of the Osmosis and Ultra-filtration of Colloidal Solutions.** WOLFGANG OSTWALD (*Kolloid Zeitsch.* 1918, **23**, 68—78).—Although the constituents of a colloidal solution appear to be separable by the expenditure of less energy than is required for the separation of solute and solvent in the case of a molecular solution, this is entirely due to the difference in the order of magnitude of the "molar" concentration of the solutions which are compared.

The methods employed in the filtration of colloidal solutions are discussed, with particular reference to the mechanical efficiency of the filters. In comparing the behaviour of colloidal solutions in respect of ultra-filtration, it is necessary to distinguish between those portions of the dispersive medium which are associated with the disperse phase in different forms. H. M. D.

**Abnormality of Strong Electrolytes. III. The Osmotic Pressure of Salt Solutions and Equilibrium between Electrolytes.** JNANENDRA CHANDRA GHOSH (T., 1918, **113**, 707—715).—By application of Clausius's virial theorem to salt solutions, it is shown that the author's theory (compare T., 1918, **113**, 449, 627) leads to the relation $i=n\{1-\frac{1}{3}\log_e 1/\alpha\}$, where $i$ represents the osmotic ratio, $n$ the number of ions resulting from a molecule of the salt, and $\alpha$ the activity coefficient.

By comparing the values of $i$ for binary and ternary electrolytes which are derived from freezing-point observations with those which are calculated (1) from the above equation, and (2) from the Arrhenius equation $i=1+(n-1)\alpha$, it is shown that the equation based on the Clausius theorem and the author's theory of electrolytes is in better agreement with the experimental results. The failure of the Arrhenius equation is very strongly marked in the case of ternary electrolytes.

It is shown that no change in the activity coefficient occurs when salt solutions of the same equivalent concentration are mixed together. H. M. D.

**Rhythmic Diffusion Structures in Gelatin-Salt Jellies. III.** W. MOELLER (*Kolloid Zeitsch.*, 1918, **23**, 11—15. Compare this vol., ii, 301).—In connexion with his theory of jelly structure, the author has made experiments with textile fabrics which indicate how, by the displacement of superposed layers of an ultramicroscopic lattice structure, rhythmic macroscopic effects may be produced. The development of a spheritic structure when hydrochloric acid is allowed to diffuse into a semi-liquid gelatin jelly containing sodium chloride is supposed to be caused by some such displacement of the lattice structure of the gelatin accompanied by hydrolytic fission, the resulting rhythmic structure being subsequently rendered visible by deposition of colloidal particles. E. H. R.

**Experiments in Rhythmic Banding.** HARRY N. HOLMES (*J. Amer. Chem. Soc.*, 1918, **40**, 1187—1195).—Silicic acid gels have been found to exhibit well-developed rhythmic banding effects when suitable electrolytes are dissolved in the gel, which is then brought into contact with aqueous solutions which react with the gel electrolyte to form insoluble compounds. Banded precipitates have thus been obtained of mercuric iodide, metallic gold, copper chromate, basic mercuric chloride, cuprous oxide, copper ferrocyanide, and basic lead iodide. The best results were obtained in the case of copper chromate, the bands and the intervening clear spaces being very sharply defined.

The formation of the rhythmically distributed bands is explained in terms of differences in the rate of diffusion. If the gel contains chromate ions and the aqueous solution copper ions, then the latter diffuse into the gel and a layer of copper chromate is formed at the surface of the gel. The chromate ions below this precipitation zone diffuse into the region which is now depleted of chromate ions and meet the advancing copper ions, whereby the thickness of the precipitation layer is increased. The difference in concentration of the chromate ions in contiguous layers is greatest just below the front of the thickening band, and in consequence the copper ions have to advance some distance beyond the band before the concentration of chromate ions is sufficiently large to cause precipitation of copper chromate and the formation of a new band. These conditions are repeated, with the production of precipitation zones in rhythmic distribution. H. M. D.

**Isomorphous Mixtures.** PAUL GAUBERT (*Compt. rend.*, 1918, **167**, 491—494).—From a general study of the properties of crystals deposited from solutions of mixtures of isomorphous salts, the author considers that the expression solid solution must be reserved for crystals, which are stable, perfectly homogeneous, and, in the case of coloured salts, almost without polychroism. Crystals formed by the regular association of very small crystals, and even in certain cases by crystalline particles themselves, must be regarded as mixed crystals. W. G.

**The Retardation of the Formation of Prussian Blue in Aluminium Hydroxide Sols.** H. FREUNDLICH and J. REITSTÖTTER (*Kolloid Zeitsch.*, 1908, **23**, 23—24).—Polemical in reply to Vorländer, this vol., ii, 301. E. H. R.

**Effect of Dissolved Substances on the Velocity of Crystallisation of Water. III.** ALBERT BRANN (*J. Amer. Chem. Soc.*, 1918, **40**, 1168—1184. Compare A., 1916, ii, 233, 424).—Further observations have been made on the influence of dissolved substances on the rate of crystallisation of water at a constant temperature of $-7{\cdot}0°$. From the results obtained with metallic chlorides and sulphates, alcohols and other related organic compounds, sugars and colloids, it would seem that the retarding influence of the dissolved substance is mainly determined by its degree of hydration. All the substances examined retard the crystallisation with the exception of colloidal ferric hydroxide, which at concentrations of 10—20 grams per litre produces an increase in the rate of crystallisation. The effects observed point to the conclusion that substances which form crystallo-hydrates are hydrated in solution to a greater extent than similar substances which crystallise in the anhydrous form. In support of the view that the velocity of crystallisation depends on the degree of hydration of the solute, a distinct parallelism is found between the velocity and the heat of solution.

Experiments made with water and potassium chloride solutions in tubes of different kinds show that the velocity of crystallisation varies directly with the diameter of the bore, but is independent of the thickness of the wall of the tube.

It is supposed that the effects produced by dissolved substances are specific in nature, but it is not yet possible to calculate from these the absolute degree of hydration. H. M. D.

**Effect of Dissolved Substances on the Velocity of Crystallisation of Formamide.** ALBERT BRANN (*J. Amer. Chem. Soc.*, 1918, **40**, 1184—1187).—Formamide is very susceptible to spontaneous crystallisation when but slightly undercooled, but it has been found possible to compare the influence of various alkali haloids on the velocity of crystallisation at −2·5°, which corresponds with an undercooling of 4·75°. The retardation of the crystallisation is supposed to be due to solvation, the extent of which appears to run parallel with the degree of hydration in aqueous solution.

For the same degree of undercooling, the velocity of crystallisation of formamide is only about one-seventh of the velocity found for water. The difference in the rates is supposed to be connected with the greater extent to which formamide is associated.

H. M. D.

**The Chemical Kinetics and Constitution of Aqueous-alcoholic Solutions of Sodium Alkyloxides.** RUD. WEGSCHEIDER (*Monatsh.*, 1918, **39**, 201—218).—A mathematical discussion of the kinetics of chemical changes between a solution of sodium in aqueous alcohol and substances which react with both sodium hydroxide and sodium ethoxide. The assumption of Lobry de Bruyn and Steger (A., 1899, i, 745; see also Senter and Wood, T., 1915, **107**, 1070), that the ratio between the amounts of sodium hydroxide and sodium ethoxide can be directly deduced from the relation between the quantities of the two reaction products, is erroneous, as also is therefore their conclusion that even in 50% alcohol the sodium is present mainly as sodium ethoxide.

D. F. T.

**Alkaline Saponification. Esterification of Citric Acids and their Glycerides.** J. PINNOW (*Zeitsch. Elektrochem.*, 1918, **24**, 270—278).—The author shows that, contrary to the statement of Meyer (this vol., ii, 223), his accounts of the esterification of triethyl citrate and the hydrogen ethyl citrates constitute the first complete work on the step-wise alkaline hydrolysis of esters of a tribasic acid. The work previously published (this vol., ii, 103) is continued in the present paper. It is shown that cotton-seed oil when treated with cold alcoholic potash is converted to the extent of 75% into the ethyl ester, whilst a small quantity is directly hydrolysed. The glycerol content in cotton-seed oil can be estimated by weighing and the use of an analytical correction. Asymmetric diethyl hydrogen citrate is hydrolysed in two ways by dilute acids. It is also shown that in preparing diethyl esters from the monoethyl esters obtained by the hydrolysis of triethyl citrate, the asymmetric diethyl ester is produced in the larger quantity. A comparison of the velocity of hydrolysis of the glycerides of acetic acid and other esters shows that the complex formation between the alkali or alcoholate does not take place with the whole ester molecule, but with dissociated groups.

J. F. S.

**Atomic Structure from the Physico-chemical Standpoint.** ALFRED W. STEWART (*Phil. Mag.*, 1918, [vi], **36**, 326—336).—The question of the structure of the atom is considered more particularly with reference to the chemical properties of the elements, and a model atom is described which takes account of the following facts: (1) the independence of the $\alpha$- and $\beta$-ray changes, (2) the difference in origin of the electrons which are involved in ordinary chemical changes and those which are ejected during $\beta$-ray changes, (3) the impossibility of controlling the ejection of $\beta$-ray electrons by any known process, (4) the alteration of the atomic number by either an $\alpha$- or a $\beta$-ray change, (5) the production of helium in an $\alpha$-ray change, (6) the difference in degree between the effects produced by the ejection of a $\beta$-ray and the corresponding change in valency produced by chemical means, (7) the possession of the same chemical properties by atoms of different weights, and, on the other hand, the identity of the weights of atoms which have different chemical properties. In this model atom, the core is negative and consists of a group of negative electrons travelling in closed orbits. Closely surrounding these are the orbits occupied by positive electrons, some of which are supposed to be associated with negative electrons. The mass of the atom is supposed to be concentrated in this zone. Further from the core, other negative electrons move in orbits of an elliptical character, the ellipses being much elongated, so that the electrons travel in paths comparable with those of comets in the solar system. When these "cometary" electrons are in a position of aphelion to the nucleus, they will be moving relatively slowly in their orbits, and hence will be less resistant to forces tending to remove them from the atom. The forces attracting the electrons towards the nucleus will also be weakest in this position, and the ease with which the valency of certain elements can be altered by chemical or electrical means can thus be readily explained. Elements which show no changes of valency may be assumed to have more nearly circular orbits for the electrons in the outer zone of the atom. For the interpretation of other properties the original must be consulted.

H. M. D.

**Romance of the Chemical Elements, their History and Etymology.** INGO W. D. HACKH (*Amer. J. Pharm.*, 1918, **90**, 478—492, 565—579).—An account of the history and the etymology of the elements. Chronological tables and family trees of related elements serve to illustrate the historical description.

H. M. D.

**Modification of the Periodic Table.** INGO W. D. HACKH (*Amer. J. Sci.*, 1918, [iv], **46**, 481—501).—A more ample account of work already published (this vol., ii, 306). C. S.

**Definition of Valency.** F. H. LORING (*Chem. News*, 1918, **117**, 319—322).—A general discussion of the meaning to be applied to the term valency. Valency is described as of four types: (1) that existing with helium atoms acting as subatomic units; this is a stronger type of valency, and consequently stronger affinity; (2) that involved in atomic combinations, that is, the ordinary valency, but with affinities which are not correlated to the valency values; (3) a residual or excess valency, which tends to become diffuse and is exerted in the formation of molecular complexes; and (4) a more remote type of valency, which, being wholly diffuse, is more of the nature of an affinity pure and simple, and in this case, which is active in cohesion, the idea of valency may be eliminated. The author supports his suggestions by extracts from various writers. J. F. S.

**Further Contributions to the Life-history of Johann Rudolph Glauber.** WALTER BRIEGER (*Chem. Weekblad*, 1918, **15**, 984—987).—A popular account, with portrait, of the life of Glauber. A. J. W.

## Inorganic Chemistry.

**Hydrogen Sulphide Generator.** T. R. ERNEST (*J. Amer. Chem. Soc.*, 1918, **40**, 1224—1226).—A compact form of generator with concentric compartments for the iron sulphide and the acid. Ease of control, absence of leakage, and large storage capacity are advantageous features claimed for the author's design.

H. M. D.

**Method of Handling Phosphorus.** BERTRAM BLOUNT (*Analyst*, 1918, **43**, 291—292).—Phosphorus may be safely handled in a vessel filled with nitrogen free from oxygen. Carbon dioxide cannot be used for this purpose, since, should the phosphorus take fire, it will continue to burn, decomposing the gas. C. A. M.

**Electrolysis of Molten Sodamide and Potassamide.** LOTHAR WÖHLER and F. STANG-LUND (*Zeitsch. Elektrochem.*, 1918, **24**, 261—270).—An open apparatus is described in which pure sodamide and potassamide may be prepared by the action of ammonia on the molten metals. The apparatus is so constructed that the physical constants of the product may be determined immediately after preparation, and the purity thereby determined. Melting points of the products were obtained from cooling curves, and the values, sodamide, m. p. 210°, potassamide, m. p. 338°, obtained, instead of the values 149—155° and 270—272°, respectively, which had been obtained previously by Titherley (T., 1894, **65**, 504). Apart from the breaks occasioned in the cooling curves by the solidification of the amides, no other breaks were observed. The method of analysis of the amides proposed by Dennis and Browne (A., 1904, ii, 558) is modified by moistening the amide with alcohol before its decomposition by water. This has the effect of making the decomposition occur more regularly. The molten amides conduct a current electrolytically, due to the ionisation $NaNH_2 \rightleftharpoons Na^{\cdot} + NH'_2$. Hydrazine is not formed at the anode as was expected, but ammonia and nitrogen, the discharge of the anion taking place according to the equation $6NH_2' + 6\oplus = 4NH_3 + N_2$. The expected formation of hydrazine was probably prevented by the catalytic action of the sodamide. Chlorine and iodine do not form hydrazine with the amides, but halogen-substituted ammonias. The specific conductivity has been determined, and the values $\kappa_{210^\circ} = 0{\cdot}593$ ohm$^{-1}$ for sodamide and $\kappa_{340^\circ} = 0{\cdot}389$ ohm$^{-1}$ for potassamide, obtained. The decomposition voltage at the melting point is found to be 0·71 volt for sodamide and 0·87 volt for potassamide, the former having a temperature coefficient $1{\cdot}52 \times 10^{-3}$ volt. J. F. S.

**Alteration in Concentrated Solutions of Sodium Hypochlorite.** M. BOUVET (*Bull. Sci. Pharmacol.*, 1917, **24**, 347—349; from *Chem. Zentr.*, 1918, i, 941).—Concentrated solutions of sodium hypochlorite rapidly lose their activity in direct sunlight. Decomposition occurs most readily in white glass flasks, considerably more slowly in vessels of brown glass. Solutions preserved in the shadow or in the dark are practically unchanged after four weeks. H. W.

**Microchemical Reactions of Metals with Rubidium and Cæsium Chlorides.** JAN VERMANDE (*Pharm. Weekblad*, 1918, **55**, 1131—1134).—An account of the preparation of double chlorides of cæsium and rubidium with mercury, silver, copper, bismuth, antimony, tin, lead, nickel, cobalt, cadmium, iron, zinc, manganese, and magnesium. These chlorides are analogous to the corresponding double salts of potassium and sodium. No double chlorides were obtained containing arsenic, aluminium, calcium, strontium, barium, potassium, sodium, or lithium. A. J. W.

**Silver Arsenide. I. Attempt to Reduce Silver Arsenate by Formaldehyde.** ENRIQUE V. ZAPPI and JUAN L. LANDABURU (*Bull. Soc. chim.*, 1918, [iv], **23**, 318—322).—Attempts to reduce silver arsenate either in the solid state or in hot or cold ammoniacal solution with formaldehyde were not successful. The product from the latter method oscillated in composition around that expressed by the formula $2Ag_3AsO_4,Ag$. W. G.

**Thermal Decomposition of certain Inorganic Trinitrides.** ARTHUR R. HITCH (*J. Amer. Chem. Soc.*, 1918, **40**, 1195—1204). —The possibility of regulating the decomposition of metallic trinitrides, when heated, has been examined in experiments conducted at different temperatures. Silver, mercurous, mercuric, barium, and thallous trinitrides decompose quickly into the corresponding elements when the temperature is suitably adjusted, but the behaviour of lead, cupric, and ammonium trinitrides is not so easily controlled. In the case of silver trinitride, which was more closely examined, quiet decomposition occurs at 280—290°. The rate of decomposition was found to increase with the temperature, and in a vacuum the evolution of nitrogen was much more rapid than at atmospheric pressure.

An arrangement of apparatus is described in which the thermal decomposition of the trinitrides may be quantitatively determined, and it is proposed to make use of this in the determination of the atomic weight of nitrogen. H. M. D.

**An Impurity of Zinc Dust.** O. BINDER (*Chem. Zeit.*, 1918, **42**, 458).—Zinc dust frequently contains a considerable amount of chlorine, and should be proved free therefrom before being used for reductions in analytical work. C. A. M.

**Basic Carbonate of Copper.** HORACE BARRATT DUNNICLIFF and SUDARSHAN LAL (T., 1918, **113**, 718—722).—The statement that commercial copper carbonate has the same composition as malachite is not in agreement with the authors' results for thirteen samples which have been examined. Attempts to prepare a basic copper carbonate of approximately constant composition have shown that a substance of the composition $2CuCO_3,5Cu(OH)_2$ may be obtained by the action of a mixture of sodium carbonate and sodium hydrogen carbonate on copper sulphate solutions.

H. M. D.

**The Rare Earths. VII. Separation of Holmium.** L. F. YNTEMA and B. S. HOPKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 1163—1167).—Experiments made with rare earth fractions containing only holmium and yttrium indicate that these may be separated by fractional hydrolysis of the phthalates. By gradually raising the temperature of the phthalate solution, basic phthalates are precipitated, and the first fractions are found to contain a larger proportion of holmium than that present in the original rare earth mixture.

Fractional precipitation by sodium nitrate from a dilute neutral nitrate solution also leads to an accumulation of holmium in the first fractions. A holmium–yttrium mixture with an "atomic weight" equal to 97·7, when separated into six fractions by this method, gave 103·3 for the "atomic weight" of the metal in the first fraction and 91·3 in the last fraction. The nitrite method is considered to promise better results than the phthalate method.

H. M. D.

**Fusion and Crystallisation of Iron-Carbon Alloys.** RUDOLF RUER and FRANZ GOERENS (*Ferrum.*, 1917, **14**, 161—177; from *Chem. Zentr.*, 1918, i, 907. Compare Ruer and Iljin, A., 1911, ii, 494; Ruer and Goerens, A., 1916, ii, 483; 1917, ii, 474). —With the object of reinvestigating certain portions of the equilibrium diagram of iron–carbon alloys, the authors have melted pure electrolytic iron with sugar carbon in an electric furnace in porcelain tubes in an atmosphere of nitrogen. The melting points of antimony (630·6°), copper (1084°), and nickel (1451°) were used for the calibration of the thermometer. The mean of the melting and solidifying points of the cementite eutectic is found to be 1145°, that of the graphite eutectic 1152°; the former alloy contains 4·2% and the latter 4·15% of carbon. The perlite point occurs at 721° with 0·9% of carbon. The authors draw the conclusion that the formation of graphite in grey pig iron occurs in the liquid phase, and that the substance separates as such from the molten mass and is not formed by the disintegration of other pre-formed crystalline varieties.

A résumé of the data which are necessary for the construction of the melting-point curves is appended. H. W.

**High Temperature Investigations. XI. Chromium and Carbon.** OTTO RUFF and THEODOR FOEHR (*Zeitsch. anorg. Chem.*, 1918, **104**, 27—46).—An account of a detailed study of the alloys of chromium and carbon. Alloys saturated with carbon were prepared by melting chromium (prepared by the alumino-thermite process and containing Al 1·33%, Fe 0·62%, Si 0·26%, $Al_2O_3$ 0·53%) in a crucible of pure carbon at temperatures varying from 1840° to 2567° for fifteen minutes, stirring frequently with a carbon rod. Samples less rich in carbon were obtained by melting a mixture of chromium and a finely powdered alloy containing 11·16% of carbon in a magnesia crucible at 1800—1850°. At higher temperatures, chromium attacks the crucible. Alumina or zirconia is no more resistant than magnesia. For the analysis of the alloys, special methods were devised, consisting in oxidising by means of potassium nitrate or sodium peroxide, carbon and chromium being converted, respectively, into carbonate and chromate.

The alloys of carbon and chromium fall into two groups: (1) those containing up to 8·5% of carbon, completely soluble in hot 24% hydrochloric acid; (2) those containing more than 8·5% of carbon, partly soluble in the same acid.

The alloys of the first group, which have been prepared containing 1·51% to 8·49% of carbon, when repeatedly extracted with cold $2N$-hydrochloric acid until no more chromium dissolves, leave a residue of practically pure $Cr_5C_2$. The low carbon alloys show a close fracture, those with a higher carbon content being coarser and showing distinct crystalline needles. Microscopic sections etched with hydrochloric acid (no other etching reagent is applicable to these alloys) show crystals of the compound embedded in a eutectic. The alloy containing 8·49% of carbon is practically pure $Cr_5C_2$ and contains no eutectic, the section showing a uniform mass of crystals. The carbide, $Cr_5C_2$, which can be prepared in quantity, forms silvery crystals, $D_4^{24·8}$ 6·915, m. p. 1665°. It is not attacked by aqua regia, and on melting undergoes no appreciable decomposition. No trace of the compound $Cr_4C$ described by Moissan was found.

The alloys of the second group, containing more than 8·5% of carbon, contain no free chromium, only carbide and graphite. The carbon content of the saturated alloys increases with the temperature of preparation, from 12·42% at 1840° to 14·03% at 2233°, and more rapidly to 23·12% at 2567°. When treated with hot 24% hydrochloric acid, part of the alloy dissolves, the ratio of chromium to carbon dissolved indicating that the soluble carbide has the composition $Cr_4C_2$. The existence of this compound could not be confirmed by isolation. The residue insoluble in hot acid contains graphite, together with the carbide, $Cr_3C_2$, which, after extraction of the graphite, is obtained 99—99·5% pure. The three constituents, $Cr_3C_2$, $Cr_4C_2$, and graphite, can be identified in microscopic sections, which show no eutectic. Possibly above 2250° a higher carbide, CrC, is formed.

The carbide, $Cr_3C_2$, is resistant to all acids. It is darker in appearance than $Cr_5C_2$, has $D_4^{21·3} = 6·683$, and melts at about 1890 ± 10°. In the molten condition, it reduces magnesia, alumina, and zirconia, and apparently undergoes partial decomposition when melted into $Cr_4C_2$ and graphite. It is decomposed by chlorine at a red heat, forming chromium trichloride and amorphous carbon.

The chemical composition of the alloys rich in carbon is unaffected by the rate of cooling, but larger crystals are developed when the rate of cooling is retarded. An alloy saturated with carbon boils at about 2570° under 8—14 mm. pressure, the vapour being pure chromium.

From the data obtained, the equilibrium diagram for the system chromium–carbon has been constructed. E. H. R.

**Metastannic Acid and its Compounds.** AUGUST KLEINSCHMIDT (*Monatsh.*, 1918, **39**, 149—178).—On account of the discrepancies in the literature concerning the action of nitric acid on tin, a reinvestigation has been made. If nitric acid is diluted with 1¼—2 volumes of water, the only product is stannous nitrate, and with stronger, and even undiluted, acid at 0—15°, the formation of stannous nitrate can still be observed, accompanied by normal or basic stannic nitrate; within the stated range of temperature, the yellowish-white precipitate which may be formed consists of a mixture of white stannic nitrate soluble in water with insoluble, yellowish-white basic stannic nitrate. Stannic nitrate even at the ordinary temperature slowly changes into the meta-salt, and for this reason the white, bulky precipitate which it yields with aqueous sodium hydroxide may not dissolve completely in an excess of the reagent; at 45°, the change in the stannic nitrate is so rapid that the solution suddenly gelatinises, and, after prolonged heating at 100°, the transformation is complete. The powdery product of oxidation of tin with hot nitric acid, commonly described as metastannic acid, is really a nitrate of metastannic acid which, on washing with water, gives rise to metastannic acid as a secondary hydrolytic product. Metastannic acid, obtained by the action of nitric acid (D 1·40) on tin and careful washing with water, when dried in air at the ordinary temperature has the composition $5H_2SnO_3,4H_2O$, the $4H_2O$ being lost on storage over sulphuric acid in a vacuum for several days; the nitric acid is removed only with difficulty, and if alcohol is used instead of water, the washing has to be still more prolonged; the primary oxidation product is therefore in all probability a metastannic nitrate which yields metastannic acid by hydrolysis. Metastannic acid shows no double refraction under the polarisation microscope and is an amorphous powder; it is capable of combining with hydrochloric acid or sulphuric acid with development of heat, the resulting compounds being very easily hydrolysable. The quinquemolecular formula for the anhydrous acid is confirmed by an analysis of sodium metastannate, produced by the action of sodium hydroxide on metastannyl chloride, the resulting compound having the composition $5SnO_2,Na_2O,4H_2O$. The parastannic acid described by Engel (A., 1898, ii, 29) is ordinary metastannic acid. Metastannic nitrate, prepared by the action of hot nitric acid on tin, has the composition $5SnO_2,2HNO_3,3H_2O$, whether dried in a vacuum over sodium hydroxide and calcium chloride or between porous tiles in the air; the compound obtained from tin and cold nitric acid probably consists of a mixture or compound of stannyl nitrate, $SnO(NO_3)_2$, and the above metastannic nitrate; both nitrates gradually decompose in ultra-violet light with liberation of nitric acid. The action of hydrochloric acid on metastannic acid yields a stannyl chloride which, after being washed free from soluble tin salts by diluted hydrochloric acid and dried in a vacuum over sodium hydroxide and calcium chloride, has the composition $5SnO_2,2HCl,3H_2O$; the primary, pasty product, on account of its content of free acid, gives a clear solution in water, but when dry does not dissolve entirely on account of hydrolysis. As simple α-stannic acid and the β-metastannic acid are colloidal substances capable of reversible inter-transformation, the change occurring more readily, however, from the α-acid to the meta-acid, these facts accord well with the respective formulæ $H_2SnO_3$ and $(H_2SnO_3)_5$; the structure of the latter is represented by a cyclic skeleton containing five tin atoms and five oxygen atoms, arranged alternately with ten hydroxyl groups attached in pairs at each tin atom. The stannyl chloride is therefore represented as $Sn_5O_5(OH)_8Cl_2$, the metanitrate as $Sn_5O_5(OH)_8(NO_3)_2$ and the metasulphate as $Sn_5O_5(OH)_8SO_4$. D. F. T.

**Presence of Vanadium and Arsenic in the Subterranean Waters of Bell-ville (Cordova).** ATILIO A. BADO (*Bol. Acad. Nac. Ciencias, Cordoba*, 1918, **23**, 85—96).—An account of analyses of water from the district of Bell-ville, in Argentina.

A. J. W.

## Mineralogical Chemistry.

**Hydrothermal Mineral Formation.** WOLF J. MÜLLER and J. KOENIGSBERGER (*Zeitsch. anorg. Chem.*, 1918, **104**, 1—26).—The investigations described in an earlier communication have been continued (A., 1906, ii, 553). The experiments have been confined to the system $K_2O$–$Al_2O_3$–$SiO_2$–$H_2O$, with or without carbon dioxide. The starting materials used were potassium silicate (potassium water glass) and an aluminium hydroxide hydrogel, or in some cases a 0·5 molar solution of potassium aluminate. Carbon dioxide was added either as potassium carbonate or as solid pellets just before closing the bomb. The several constituents in the proportions required were heated for varying lengths of time (12 to 180 hours) at temperatures varying from 100° to 440° in a strongly made bomb. Inside the bomb was a filter tube, so arranged that by inverting the furnace the liquid contained in the bomb could be filtered into this tube, and any crystals separating subsequently collected and examined. The products were identified generally by optical methods.

On few occasions were any crystals obtained in the filter tube, the only products identified being quartz, orthoclase, zeolite, and pectolite, not leucite or nepheline. With rising temperature, the quantity of leucite in the solid phase diminishes, that of orthoclase increasing. From the slight amount of filter-tube product obtained, it is clear that the concentration of potassium aluminium silicate in the water at the temperatures employed is low, and is not likely appreciably to affect the critical temperature of the water.

Potassium felspar was only identified when the temperature used was 360° or above. This critical temperature (360 ± 20°) should be an important fixed point for the geological thermometer. The presence of carbon dioxide or of sodium or calcium ions introduced in the form of labradorite does not affect the critical temperature. Albite was not observed up to 430°, but Baur has obtained it under similar conditions at 450° (A., 1911, ii, 991). In presence of carbon dioxide at 310°, quartz alone is stable, the aluminosilicates appearing to be transitional with short heating at lower temperatures, forming again with longer heating at higher temperatures. The succession of minerals observed in nature is in better agreement with the results of experiments in which much carbon dioxide was present than in those without.

The formation of zeolites in absence of carbon dioxide commences below 100° and may increase up to 400°, but probably their limit of stability, with the exception of analcime, is below 300°.

The opinion is confirmed that, in hydrothermal syntheses below 400°, equilibrium is seldom attained. E. H. R.

**Meteoric Iron from Chili (Dehesa).** F. BERWERTH (*Tsch. Min. Mitt.*, 1917, **34**, 272).—This mass was described by Daubrée in 1868, and was stated by Domeyko to have been found in the Cordillera de la Dehesa, near Santiago. From its compact appearance and Domeyko's analysis (Ni 14%), it was placed in the group of nickel-rich 'compact irons.' Microscopical examination of an etched surface shows, however, that the structure is octahedral. The following new analysis (mean of two by E. DITTLER) was therefore made, showing that this iron belongs to the group of very fine octahedrites.

| Fe. | Ni. | Co. | Insol. (Schreibersite). |
|---|---|---|---|
| 87·40 | 11·97 | 0·56 | 0·07 |

L. J. S.

## Analytical Chemistry.

**Calculation of the Possible Error in Gravimetric Estimations.** V. ZOTIER (*Bull. Sci. Pharmacol.*, 1917, **24**, 298—302; from *Chem. Zentr.*, 1918, i, 945).—In the gravimetric estimation of the amount, $x$, of a substance, $X$, dissolved in water by conversion into an insoluble substance, $Y$, and weighing the quantity of the latter, $y$, the possible total error, exclusive of that due to the personal factor, is exactly equal to the algebraic sum of the individual errors. If $m_1$ and $m_2$ are the molecular weights of $X$ and $Y$, respectively, $\Delta m_1$ and $\Delta m_2$ the accuracy of their determination (the value O=16 being considered exact as fundamental), the relative error is expressed by the following relationship:

$$\Delta x/x = (m_2 y \,.\, \Delta m_1 + m_1 y \,.\, \Delta m_2 + m_1 \,.\, m_2 \Delta y)/(x \,.\, m^2_2).$$

The estimation of sulphuric acid by weighing the barium sulphate formed is chosen as example; the possible sources of error are the solubility of the sulphate in water, adhesion of the precipitate to the glass, adhesion of foreign matter to the precipitate, the weight of dust falling on the precipitate during the estimation, increase in weight of the crucible by deposition of moisture, errors in weighing, and loss during incineration. Of these, the solubility and the error in weighing can be mathematically treated; the others are, in part, independent of *y*, and their sign and magnitude can only be arbitrarily estimated. In the case given above, the uncertainty is calculated to be 11:1000. H. W.

**Colorimetric Determination of the Reaction of Bacteriological Media and other Liquids.** G. D. Barnett and H. S. Chapman (*Amer. J. Pharm.*, 1918, **90**, 592—595).—The method depends on the superimposing of two extreme colours of the indicator, as first proposed by Salm (A., 1906, ii, 218). For example, in the case of a phenolsulphonephthalein solution, the observed colour may be regarded as being composed of a definite amount of red with a definite amount of yellow, and may be matched by superimposing the extreme red and extreme yellow of the indicator in proper concentrations. If five drops of a solution of this indicator be added to a tube containing 5 c.c. of dilute acid, and five drops to another tube containing 5 c.c. of dilute alkali, the colour observed by transmitted light through both tubes will be half-way between the yellow and the red. This is the half-transformation point, and is a definite constant for this indicator. By partitioning the ten drops of indicator in varying proportions between tubes containing the same amounts of acid and alkali, and viewing each pair by transmitted light, a series of colours covering the range of usefulness of this indicator (6·9 to 8·1 $p_H$) will be obtained. By standardising the series by comparison with solutions of known hydrogen-ion concentration, it may be used as a colour standard for the determination of unknown reactions. C. A. M.

**Simple Application of the Volhard Principle for the Estimation of Chlorides in Blood Plasma.** W. C. Rappleye (*J. Biol. Chem.*, 1918, **35**, 509—512).—The citrated plasma is diluted with water, the chlorides precipitated by a standard solution of silver nitrate, and, after filtration, the excess of silver titrated by potassium thiocyanate, using iron ammonium alum as an indicator. Employing a silver nitrate solution of such a strength that 1 c.c. is equivalent to 2·5 mg. of sodium chloride, and a thiocyanate solution of one-fifth of the strength of the silver nitrate solution, the error in the estimation of the chlorides in 2 c.c. of the plasma does not exceed 1%. H. W. B.

**Important Alteration in a Sodium Thiosulphate Solution.** H. I. Waterman (*Chem. Weekblad*, 1918, **15**, 1098—1099).—From May to August, the strength of a sodium thiosulphate solution, as determined by the iodine method, altered from 0·923 × *N*/10 to 1·021 × *N*/10. The author is unable to suggest an explanation of the phenomenon. A. J. W.

**Simplified Gasometric Estimations.** ANDRÉ RENAUD (*J. Pharm. Chim.*, 1918, [vii], **18**, 104—106).—To avoid frequent standardisations of the nitrometer in the estimation of nitrogen in urea, a second tube, exactly similar to the nitrometer tube, is employed. A known amount of urea is decomposed as usual in the nitrometer, and the volume of nitrogen obtained is noted. The same volume of air is then admitted to the comparison tube, and this volume is used as the standard in subsequent estimations. [See, further, *J. Soc. Chem. Ind.*, November.] W. P. S.

**A Survey of Methods for the Estimation of Nitrites and Nitrates in the same Solution.** ALICE OELSNER (*Zeitsch. angew. Chem.*, 1918, **31**, 170—172, 178—179).—The various methods available for the estimation of nitrites and nitrates in presence of each other are reviewed. The colorimetric methods are suitable for water analysis. The diphenylamine–sulphuric acid reagent is available for both nitrates and nitrites, since, when diluted with a definite volume of water, it ceases to react with nitrates and shows a blue colour with nitrites. The nitrites are estimated first and then destroyed with urea and sulphuric acid or by boiling with ammonium chloride; this treatment does not affect the nitrates. Letts and Rea (T., 1914, **105**, 1157) recommend diphenylbenzidine. Several gasometric methods have been described, depending on the evolution and measurement of nitrogen or nitric oxide. For instance, on boiling a nitrite with ammonium chloride, nitrogen is evolved equivalent to twice that of the nitrite; the presence of nitrate has no influence. Ferrous chloride in presence of acetic acid or ferrous ammonium sulphate alone, on boiling, decompose nitrites with evolution of nitric oxide, which may be measured in a eudiometer. The subsequent addition of hydrochloric acid to the same solution causes the decomposition of the nitrates according to Schlœsing's method. Nitric oxide may also be liberated first by hydriodic acid, which decomposes nitrites, and then by ferrous chloride and hydrochloric acid, which decomposes nitrates. Winogradsky prefers to estimate the nitrites by titration with permanganate, with the formation of nitrate, and then the total nitrates by Schlœsing's method. In the analysis of culture media for the study of the progress of nitrification and denitrification by bacteria, the author recommends the permanganate method, the solution of nitrite being titrated into the diluted permanganate, previously acidified and warmed to 40°. Towards the end of the titration, plenty of time must be allowed between each addition, as the oxidation is somewhat slow. The total nitrogen is then determined as ammonia after reduction by zinc and iron in alkaline solution. The method gives much closer results than Winogradsky's, and is applicable to culture liquids which do not contain ferrous sulphate, which, moreover, is not essential for the growth of these bacteria.

The culture media may contain small quantities of other reducing substances which involve a constant error, generally negligible.

Citric acid is generally employed, but does not affect the nitrite titration performed in the manner described. Ammonium salts are eliminated by boiling before reduction of the total nitrate. Franzen and Löhman (A., 1909, ii, 517) have criticised the gasometric methods as applied to bacteriological work, and recommend Busch's method (A., 1906, ii, 392) for liquids containing much organic matter, based on oxidation of nitrites by peroxide and their decomposition by hydrazine sulphate, the nitrates being determined in both portions by precipitation with nitron. Methods of minor importance have been based on the precipitation of nitrites by 2 : 4-diamino-6-hydroxypyrimidine sulphate, and on the elimination of nitrites by esterification with methyl alcohol in presence of standard hydrochloric acid, the loss of acidity being determined. J. F. B.

**Gravimetric Estimation of Phosphates.** W. R. Mummery (*Analyst*, 1918, **43**, 324).—Complete precipitation of phosphoric acid may be effected by a modification of Ullmann's method, in which the nitric acid solution is filtered prior to dilution to a standard volume. Phosphomolybdates are precipitated at 60° and allowed to remain for thirty minutes at 60°, whilst magnesium ammonium phosphate is precipitated at 80° and left for three hours at the ordinary temperature. C. A. M.

**The Estimation of Phosphoric Acid as Magnesium Pyrophosphate. IV.** D. Balareff (*Zeitsch. anorg. Chem.*, 1918, **104**, 53—56).—On account of the slight solubility of the two phosphates $Mg[(NH_4)_2PO_4]_2$ and $Mg_3(PO_4)_2$, it is practically impossible to get true equilibrium in solution and is difficult to obtain a pure precipitate of normal magnesium ammonium phosphate (compare this vol., ii, 332). When the velocity of precipitation is retarded by allowing ammonia to diffuse slowly into an acid solution of the phosphoric acid–magnesia mixture in presence of ammonium chloride in the cold, the precipitate is practically pure $MgNH_4PO_4$. Experiments on the method of Schmitz, by which ammonia is added to a hot solution in presence of ammonium chloride and precipitation occurs on cooling, show that the precipitate thus produced is not pure. On ignition, part of the phosphoric acid is lost by volatilisation, and the residue is relatively rich in magnesium and poor in phosphoric acid, the errors approximately compensating one another. It is therefore inadvisable to redissolve and reprecipitate after ignition. The result obtained by this method is not affected by variations in dilution or in the quantity of ammonium chloride present. E. H. R.

**Rapid Micro-method for the Estimation of Phosphate and Total Phosphorus in Urine and Stools.** Akira Sato (*J. Biol. Chem.*, 1918, **35**, 473—477).—The phosphate is precipitated by uranium in the presence of sodium acetate and acetic acid, alcohol being added to facilitate precipitation and filtration.

The uranium phosphate is then dissolved in acid and the solution treated with potassium ferrocyanide. A red colour is developed, the intensity of which is compared in a colorimeter with that produced in a similar manner from a standard uranium phosphate solution in hydrochloric acid. H. W. B.

**Use of Manna in the Estimation of Boric Acid.** LILLIAN E. ILES (*Analyst*, 1918, **43**, 323).—A freshly prepared solution of manna can replace glycerol in the estimation of boric acid. As a rule, about 5 grams of manna in solution are equivalent to about 25 c.c. of 80% glycerol. C. A. M.

**Estimation of Silicon in Ferrosilicon.** P. NICOLARDOT and J. KOENIG (*Ann. Chim. anal.*, 1918, **23**, 169—173).—The ferrosilicon is fused with sodium carbonate and potassium nitrate, and the silica then estimated by the usual methods. W. P. S.

**Estimation of Total Carbon in Various Biological Substances.** ANDRÉ RENAUD (*J. Pharm. Chim.*, 1918, [viii], **18**, 106—108).—The substance is heated with sulphuric acid and potassium dichromate, and the resulting carbon dioxide, together with other gases, is absorbed in ammoniacal calcium chloride solution. The resulting calcium carbonate is then estimated volumetrically. If ammoniacal barium carbonate is used for the absorption, the barium carbonate obtained may be converted into barium sulphate and weighed as such. [See, further, *J. Soc. Chem. Ind.*, November.] W. P. S.

**Estimation of Potassium.** THOS. STEEL (*Analyst*, 1918, **43**, 348—349).—The hydrochloric acid solution containing the potassium, and also iron, calcium, magnesium, etc., but free from silica, is evaporated with the addition of an excess of platinum chloride, and the residue obtained is treated with a mixture of alcohol, 76, ether, 13, water, 11 parts. The precipitate is collected, washed with the alcohol–ether–water mixture, then dissolved in boiling water, and the solution boiled with an excess of sodium formate; after a few minutes, hydrochloric acid is added, the heating continued until the reduced platinum has flocculated, and the platinum then collected, washed, ignited, and weighed.
W. P. S.

**Volumetric Estimation of Barium and the Solubility of Barium Chromate in Various Aqueous Solutions.** JOHN WADDELL (*Analyst*, 1918, **43**, 287—289).—Barium chromate, as obtained in the separation of strontium and calcium, may be determined by a method analogous to that used for lead.

The precipitate of barium chromate (about 0·15 gram) is collected on asbestos in a Gooch's crucible and dissolved in 25 c.c. of strong hydrochloric acid and 75 c.c. of water, and the solution made up to 200 c.c. About 6 grams of potassium iodide are added, and, after ten minutes, the liberated iodine is titrated with standard thiosulphate solution. It is essential that the hydrochloric acid should be cold and dilute to prevent liberation of chlorine by the chromate. The method has been used to determine the solubility of barium chromate in water and various aqueous solutions under the ordinary conditions of washing a precipitate. The results showed that for washing barium chromate, pure water is preferable to 1% ammonium acetate solution, which dissolves about four times as much of the salt as water. C. A. M.

**Method for the Separation and Estimation of Barium Associated with Strontium.** F. A. GOOCH and M. A. SODERMAN (*Amer. J. Sci.*, 1918, **46**, 538—540).—Barium and strontium may be separated by treating the saturated solution of their chlorides with a mixture of concentrated hydrochloric acid and ether (4 : 1); about 50 c.c. of this mixture are required for 0·5 gram of the mixed salts. The precipitated barium chloride is then collected on an asbestos filter, washed with the hydrochloric acid–ether mixture, dried at 150°, and weighed. [See, further, *J. Soc. Chem. Ind.*, November.] W. P. S.

**Volumetric Estimation of Zinc.** R. HOWDEN (*Chem. News*, 1918, **117**, 322).—Zinc can be estimated volumetrically as chloride and in the absence of salts of ammonium and the heavy metals in the following way. The solution is evaporated to remove most of the free acid and then exactly neutralised by *N*/10-sodium hydroxide, using one drop of methyl-orange as indicator. The solution is then titrated further with *N*/10-sodium hydroxide, using phenolphthalein as indicator. Towards the end of the titration, the solution is boiled, and the end-point taken as that point where the pink colour remains on boiling. The method is stated to give absolutely concordant results. J. F. S.

**Analysis of Commercial Zinc.** L. BERTIAUX (*Ann. Chim. anal.*, 1918, **23**, 161—169, 181—191).—Methods are described in detail for the estimation of the following impurities in commercial zinc: lead, iron, cadmium, sulphur, carbon, copper, arsenic, and antimony. Analyses of forty-two samples are recorded. The maximum amount of copper found was 0·012%, of tin 0·576%, of iron 0·210%, of lead 2·327%, of cadmium 0·380%, of sulphur, trace, and of carbon 0·033%. Arsenic and antimony were present in traces only. [See, further, *J. Soc. Chem. Ind.*, 658A.] W. P. S.

**Separation of Traces of Copper from Solution.** J. E. SAUL and DAVID CRAWFORD (*Analyst*, 1918, **43**, 348).—The antiseptic known as quinosol (the potassium salt of 8-hydroxyquinoline-5-sulphonic acid) gives a precipitate with traces of copper. If 0·1 gram of quinosol is dissolved in 100 c.c. of water containing 0·0002 gram of copper (as a salt), a voluminous, yellow precipitate forms within eighteen hours; the precipitate is soluble in dilute hydrochloric acid. By means of this reagent, copper may be detected in distilled water which has been stored in copper vessels. Other metals in very dilute solution do not give a reaction, but a precipitate may be obtained from a concentrated solution of a mercuric salt. W. P. S.

**The Detection of Mercury in Urine, with Employment of a New Solvent for Mercuric Sulphide.** S. Gutman (*Biochem. Zeitsch.*, 1918, **89**, 199—203).—The solvent in question is a solution of hydriodic acid, prepared by dissolving 5 grams of potassium iodide in 12 c.c. of 10% sulphuric acid, and diluting to 25 c.c. The urine is treated first with hydrochloric acid and potassium chlorate to destroy the organic matter. From the slightly acid solution, mercury is precipitated by hydrogen sulphide. The sulphide is purified by dissolving in aqua regia and reprecipitation with hydrogen sulphide. This precipitate, if it is mercuric sulphide, should be insoluble in hot nitric acid solution, but soluble in aqua regia and the given solution of hydriodic acid. S. B. S.

**Adsorption of Colloidal Hydroxides.** K. Scheringa (*Pharm. Weekblad*, 1918, **55**, 1070—1074).—The author considers that in analysis the adsorption of ordinary salts by metallic hydroxides has not much practical significance. In separating iron, a large excess of alkali is undesirable. A. J. W.

**Precipitation of Iron by Hydrogen Sulphide.** R. Winderlich (*Zeitsch. physikal. Chem. Unterr.*, 1917, **30**, 254; from *Chem. Zentr.*, 1918, i, 814).—It is commonly stated that hydrogen sulphide does not produce a precipitate in solutions of ferrous salts. This is so only in solutions in mineral acids. Even Gay-Lussac mentioned that in the presence of sodium acetate a precipitate of ferrous sulphide is obtained. Ferrous sulphide is also precipitated from solutions of ferrous acetate in acetic acid and of iron powder in citric or succinic acid. C. S.

**Use of Titanium Trichloride as a Reducing Agent in the Estimation of Iron by Titration with Permanganate in Hydrochloric Acid Solution.** L. Brandt (*Chem. Zeit.*, 1918, **42**, 433—434, 450—451).—Titanium trichloride solution may be used in place of stannous chloride solution for the reduction of ferric salts previous to the titration of the latter with permanganate solution. The ferric salt may be reduced by the addition of exactly the requisite quantity of the titanium trichloride solution, or an excess may be added, and this excess then removed by means of copper sulphate. The presence of platinum chloride, potassium dichromate, or arsenic acid in the ferric salt solution does not affect the results. Copper sulphate may also be used for removing excess of stannous chloride when this is employed for reducing the ferric salt. W. P. S.

**The Colorimetric Estimation of Cobalt.** E. GABRIEL JONES (*Analyst*, 1918, **43**, 317—319).—Small quantities of cobalt (0·01 to 0·1%) may be colorimetrically estimated by means of a solution of α-nitroso-β-naphthol, as used by Atack (A., 1915, ii, 652), ammonium citrate solution being added to eliminate the effect of moderate quantities of many other metals. In the case of varnishes, a solution of the ash from the sample in hydrochloric acid is treated with the reagents, and the coloration compared with those given by different quantities of a standard solution of cobalt containing the same amounts of ammonium citrate and α-nitroso-β-naphthol. About 0·1 mg. of cobalt is the most satisfactory quantity for the comparison. It is essential that the solutions should contain about the same amount of free ammonia. Iron, zinc, and lead do not interfere with the estimation, but copper, nickel, or manganese, if present in notable quantities, must be removed prior to the estimation. C. A. M.

**Estimation of Tin in High-grade Wolfram Ores, and the Use of Lead as a Reduction Agent in Pearce's Assay.** A. R. POWELL (*J. Soc. Chem. Ind.*, 1918, **37**, 285—287T).—One gram of the finely ground sample is added to 5 grams of fused "bisulphate," the mixture heated to redness, then cooled, and boiled with about 80 c.c. of 5% tartaric acid solution. The insoluble portion is collected, washed with hot water, ignited while wet in an iron crucible and fused with sodium peroxide, and the tin estimated in the usual way. Traces of tin remaining in the tartaric acid solution may be recovered by means of hydrogen sulphide. The results obtained are trustworthy and agree with those found by the aqua regia method, the potassium cyanide fusion method, and the sodium peroxide fusion method. Lead may be used for the reduction of stannic salts. The solution from the sodium peroxide fusion is rendered slightly acid with hydrochloric acid, diluted to 100 c.c., 20 grams of sodium chloride, 40 c.c. of concentrated hydrochloric acid and 10 grams of granulated lead are added, and the solution is boiled for twenty minutes after the disappearance of the ferric chloride colour. A piece of marble is then added, the solution cooled, diluted with 50 c.c. of dilute sodium hydrogen carbonate solution, and titrated with iodine solution without removing the excess of lead. W. P. S.

**Quantitative Estimation of Vapours in Gases. A Differential Pressure Method.** HAROLD S. DAVIS and MARY DAVIDSON DAVIS (*J. Ind. Eng. Chem.*, 1918, **10**, 709—712).—The method depends on the fact that the vapour pressure from a liquid is independent of the kind of gas above it, provided the gas is inert (Dalton's law of partial pressure); deviations from this law are known, but it holds in the case of benzene and air. If two flasks are connected by a manometer, one of the flasks containing air and the other a mixture of air and benzene vapour corresponding with a pressure less than the saturation pressure, and a small bulb of benzene is broken in each flask, the liquid benzene in the second flask will add only the amount of pressure necessary to bring its pressure up to saturation; the benzene in the flask containing air only will, however, produce the total saturation pressure, and the manometer will register a difference in pressure equal to the pressure of the vapour in the original gas mixture. W. P. S.

**Application of the Differential Pressure Method to the Estimation of Benzene and the Total Light Oil Content of Gases.** HAROLD S. DAVIS, MARY DAVIDSON DAVIS, and DONALD G. MACGREGOR (*J. Ind. Eng. Chem.*, 1918, **10**, 712—718).—Details of procedure are given for the application of this method (preceding abstract) to the estimation of benzene, toluene, and xylene in gases. W. P. S.

**Absorption of Light Oils from Gases.** HAROLD S. DAVIS and MARY DAVIDSON DAVIS (*J. Ind. Eng. Chem.*, 1918, **10**, 718—725).—The vapour pressure of benzene from its solution in oil is governed by Henry's law for the solubility of gases in liquids and by Babo's law for the constancy of the fractional lowering of the vapour pressure from a solution over variations in temperature, and the flow of oil necessary to remove completely the benzene from a gas may be calculated accordingly. Determination of the molecular weight of an oil when dissolved in benzene is suggested as a method for standardising oils as regards their efficiency for absorbing vapours from gases. W. P. S.

**Estimation of Alcohol in Spirituous Liquors.** NAGENDRA CHANDRA NAG and PANNA LAL (*J. Soc. Chem. Ind.*, 1918, **37**, 290T).—A known weight of the alcoholic liquid is treated in a graduated cylinder with an excess of anhydrous potassium carbonate, 5 to 10% of water being added if the alcohol content is more than 90%; the mixture is then shaken and allowed to remain, or it may be subjected to centrifugal action. It separates into three layers: a lower layer of solid potassium carbonate, a middle layer of saturated potassium carbonate solution, and an upper layer of alcohol hydrate, $4C_2H_5\cdot OH,H_2O$, which contains 94·061% of alcohol by volume or 91·089% by weight. The percentage quantity of alcohol in the sample is

$$(V + v \times 0{\cdot}00275)[1 - 0{\cdot}001068(t - 15{\cdot}6)] \times 0{\cdot}7936 \times 94{\cdot}06 / W.$$

$V$ is the volume, in c.c., of the alcohol hydrate observed, $v$ the volume of the saturated potassium carbonate solution, $t$ the temperature, $W$ the weight in grams of the sample taken, 0·00275 is the solubility (in c.c.) of the alcohol hydrate per c.c. of the saturated potassium carbonate solution, 0·001068 the apparent coefficient of expansion of alcohol hydrate, and 0·7936 is the $D_{15\cdot 6}^{15\cdot 6}$ of absolute alcohol. W. P. S.

**A New Reaction for Acetylcarbinol.** OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1918, **89**, 279—280).—A dilute solution of acetylcarbinol in water containing sodium hydroxide is boiled for a few minutes with *o*-aminobenzaldehyde. The mixture is then cooled, acidified, and made alkaline again with sodium hydrogen carbonate. A fluorescent solution is obtained, from which 3-hydroxy-2-methylquinoline can be extracted by ether; on distilling off the ether, it is obtained as a white residue, which gives a deep red colour with ferric chloride in alcoholic solution. The alcoholic solution also gives a brilliant blue fluorescence on dilution with water. These two reactions are characteristic.

S. B. S.

**The Detection of Sucrose in Milk.** G. D. ELSDON (*Analyst*, 1918, **43**, 292—293).—The most sensitive test for sucrose in milk is a modification of Gayaux's test, in which 15 c.c. of the milk are treated with 1 c.c. of $3N$-hydrochloric acid and 0·5 gram of resorcinol. On drying five drops of the resulting mixture on a white tile on the water-bath, a red coloration is obtained in the presence of as little as 0·02% of sucrose. C. A. M.

**Titration of Oxalic Acid by the Conductance Method.** HERBERT S. HARNED and CLINTON N. LAIRD (*J. Amer. Chem. Soc.*, 1918, **40**, 1213—1218).—The electrical conductivity method affords a means of titrating a strong acid in presence of much weaker acids, and as a result of observations on the change of conductivity which occurs when a solution of oxalic acid is titrated with sodium hydroxide, it is found that the replacement of the first hydrogen atom by sodium is indicated very sharply by the conductivity. The influence of dilution on the sharpness of the change in the conductivity at the point at which the acid oxalate is formed has been examined, and it appears that the abruptness of the change increases with the dilution. The presence of carbonate in the hydroxide solution leads to high results when the conductance method is used in the estimation of oxalic acid. [See, further, *J. Soc. Chem. Ind.*, 653A.] H. M. D.

**Separation of Oxalic Acid from Tartaric Acid.** ARMINIUS BAU (*Chem. Zeit.*, 1918, **42**, 425—426).—The solution, containing not more than 0·2% of oxalic acid, is treated with boric acid and one-fifth of its volume of calcium acetate solution, the mixture is kept in an ice-chest for forty-four hours, the precipitate of calcium oxalate then collected, washed, ignited, and the resulting calcium oxide titrated with $N/10$-hydrochloric acid. The volume of the filtrate and of the wash water must be noted; the solubility of calcium oxalate in the filtrate is equivalent to 3·42 mg. of oxalic acid per litre, whilst in the wash water it is equivalent to 4·64 mg. of oxalic acid per litre. The weight of oxalic acid found is corrected accordingly. The calcium acetate solution used is made by adding 500 c.c. of a solution of 330 grams of sodium acetate in 300 c.c. of water to 25 grams of calcium chloride dissolved in 500 c.c. of 50% acetic acid; the mixture is kept at 7° for forty-eight hours, and then filtered. The amount of boric acid required to prevent the precipitation of calcium tartrate is at least 0·25 mol. of boric acid expressed in terms of tartaric acid, but a large excess of boric acid does not interfere. W. P. S.

**Detection and Identification of Malonic Acid.** BOUGAULT (*Ann. Chim. anal.*, 1918, **23**, 154—155).—Malonic acid condenses with cinnamaldehyde to form cinnamylidenemalonic acid, a yellow compound, m. p. 208°, practically insoluble in water (compare Riiber, A., 1904, i, 894). A mixture of 0·10 gram of malonic acid (or an equivalent quantity of its sodium or calcium salt), 15 drops of cinnamaldehyde, and 1 c.c. of acetic acid is heated at 100° in a sealed tube for ten hours. The mixture is then diluted with 15 c.c. of water, the solution saturated with sodium carbonate, filtered, and the filtrate acidified with hydrochloric acid; the yellow precipitate formed is collected, dried at 100°, and weighed. Each gram of malonic acid yields approximately 1·10 gram of cinnamylidenemalonic acid. Oxalic acid, succinic acid, citric acid, sodium chloride, or potassium sulphate do not interfere with the reaction. W. P. S.

**Estimation of Indigotin.** WILHELM HEINISCH (*Färber-Zeit.*, 1918, **29**, 183—184, 194—197).—The most suitable method for the estimation of indigotin in indigo is by titration with permanganate. Constant values for the oxygen consumed are only obtained by performing the titration in highly dilute solutions, from 1 part of indigotin in 20,000 of water, onwards. The constant value does not represent the oxidation of 1 molecule of indigotin by 2 atoms of oxygen with the formation of isatin, as was formerly supposed, but corresponds with the production of a complex oxidation product resulting from the action of 9 atoms of oxygen on 5 molecules of indigotin. Thus 262 parts of indigotin require 28·8 parts of oxygen, or, in other words, 1 mg. of potassium permanganate oxidises 2·3 mg. of indigotin. Using this ratio as the basis of the standard permanganate solution, it is possible to dispense with the usual practice of standardising the permanganate against a sample of indigotin of known purity; ferrous ammonium sulphate or an oxalate may be employed. The residual colour of the oxidised indigo solution ranges from yellow to reddish-brown, and the exact end-point cannot be established by ordinary direct titration. Accurate results may, however, be obtained by a process of colour matching. The titration is carried out simultaneously in duplicate nearly to the end-point, a faint green. Permanganate is then added alternately in small quantities to each of the solutions, which are compared against a white ground after each addition, until one sample shows no green tone and the other still retains a visible trace. [See, further, *J. Soc. Chem. Ind.*, 648A.] J. F. B.

**Colour Reaction of Mercury Fulminate with Phenylhydrazine.** A. LANGHANS (*Zeitsch. angew. Chem.*, 1918, **31**, i, 161—163).—On treating mercury fulminate with phenylhydrazine, decomposition takes place, and on subsequently diluting the liquid with alcohol and adding a dilute acid, preferably sulphuric acid, a reddish-violet coloration is produced. This reaction may be used as a sensitive test for mercury fulminate. The dye can be extracted with chloroform, and its reactions indicate that it is pararosaniline. It is probable that the mercury plays a part in the reaction, since several mercury salts have been used in the preparation of rosaniline.

When phenylhydrazine is decomposed with chloride of lime, crystals of azobenzene and a yellowish-brown oil are produced. The oil consists of benzene, azobenzene, and aniline:

$$2NHPh\cdot NH_2+3O=3H_2O+N_2+NPh{:}NPh,$$
$$2NHPh\cdot NH_2+2O=2H_2O+2N_2+2C_6H_6.$$

[See also *J. Soc. Chem. Ind.*, 1918, 637A.] C. A. M.

**Simple Apparatus for the Estimation of Urea in Blood.** C. N. PELTRISOT (*J. Pharm. Chim.*, 1918, [vii], **18**, 73—80).—A small nitrometer is described for the estimation of nitrogen by the hypobromite method; it is constructed from a 30 c.c. glass bottle and a piece of graduated tubing, 8 cm. in length and 7 mm. in diameter. W. P. S.

**Estimation of Creatinine and Creatine in Blood.** W. DENIS (*J. Biol. Chem.*, 1918, **35**, 513—516).—Accurate results for creatine and creatinine in the blood can be obtained by Folin's method (A., 1914, ii, 505) if the proteins are first precipitated by metaphosphoric acid. H. W. B.

**Detection of Ergotinine.** LUDWIG WOLTER (*Chem. Zeit.*, 1918, **42**, 446).—An alcoholic solution of ergotinine containing 1 part in 1,240,000 gives a distinct reaction with the potassium mercuric iodide reagent for alkaloids. The yellowish-red zone, changing to violet and then to blue, given by a solution of ergotinine on the addition of sulphuric acid, is characteristic of this alkaloid (Tanret). In Rosenthaler's and in Keller's modifications of the test, a trace of ferric chloride is present. It is essential that all these tests, and especially that of Tanret, should be applied under definite conditions, and in particular that the solution of the alkaloid must not be too concentrated, or zones of other colours than blue will be obtained. The hypothesis that the coloration is due to oxidation was confirmed by the fact that a trace of hydrogen peroxide could replace ferric chloride in the test. With this modification, the reaction is rendered twice as sensitive as Tanret's original test. [See also *J. Soc. Chem. Ind.*, 1918, 671A.]

C. A. M.

**The Value of Tanret's Reagent for the Detection of Quinine in Urine.** G. PÉPIN (*Bull. Sci. Pharmacol.*, 1917, **24**, 337—338; from *Chem. Zentr.*, 1918, i, 955).—Tanret's reagent is unsuitable for the detection of quinine in urine, since it yields precipitates which are soluble when warmed, even in the absence of proteins and alkaloids. H. W.

**Isolation and Estimation of Small Quantities of Quinine in Urine.** G. PÉPIN (*Bull. Sci. Pharmacol.*, 1918, **25**, 19—22; from *Chem. Zentr.*, 1918, i, 955).—The quinine is isolated by repeated extraction with small quantities of chloroform, purified, and dissolved in a few c.c. of water acidified with hydrochloric acid; the alkaloid is converted into a derivative which is soluble in water, and estimated by measuring the quantity of the solvent necessary for complete solution. The hydrate is suitable for amounts of 2—3 mg. and upwards, the picrate for quantities of less than 1 mg. Distinct fluorescence is observed with more than 1/20 mg. dissolved in water (2 c.c.). The presence of antipyrine and pyramidone alter the fluorescence and solubility of the picrate. H. W.

**Estimation of Purine Bases in Food-stuffs.** TH. VON FELLENBERG (*Biochem. Zeitsch.*, 1918, **88**, 323—336).—The author describes in detail the method employed, the bases being precipitated by copper sulphate and sodium hydrogen sulphite, and the nitrogen estimated in the precipitate. The purine content of a large number of foodstuffs is given. S. B. S.

**Combined Estimation of Tyrosine and Uric Acid in the same Solution.** E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, **88**, 283—285).—Folin's phenol reagent is employed. It gives a colour twice as strong with tyrosine as with uric acid. The colour with the solution of the two substances is first estimated, then uric acid is destroyed by hydrogen peroxide and sodium hydroxide, then the phenol reagent is added again, under conditions specified, and the tyrosine alone is determined colorimetrically. S. B. S.

**Detection of Bile Pigments in Serum.** A. FOUCHET (*Compt. rend. soc. biol.*, 1917, **80**, 826—828; from *Physiol. Abstr.*, 1918, **3**, 246—247).—Proteins are precipitated by trichloroacetic acid, and the precipitate is yellow if bile pigments are present. On exposure to air, the precipitate becomes green, the oxidation to biliverdin being accelerated by the addition of ferric chloride. The method may be used colorimetrically. S. B. S.

**Modification of Grimbert's Method for the Detection of Biliary Pigments in Urine.** A. FOUCHET (*J. Pharm. Chim.*, 1918, [vii], **18**, 19—20).—Ten c.c. of the urine are treated with 3 c.c. of 10% barium chloride solution, the mixture submitted to centrifugal action, the sediment washed, and then mixed with 1 c.c. of a reagent consisting of trichloroacetic acid, 3 grams, ferric chloride solution, 2 c.c., and water, 20 c.c. A green coloration develops within a few minutes if biliary pigments are present. The sensitiveness of the test is about 1 in 50,000. W. P. S.

**Detection of Methylene-blue in Urine.** L. Tribondeau (*Compt. rend. soc. biol.*, 1917, **80**, 882; from *Physiol. Abstr.*, 1918, **3**, 264).—Urine is acidified with acetic acid, fragments of thymol are added, and the mixture is boiled. Thymol collects on the surface, carrying with it the pigment. S. B. S.

**Approximate Estimation of Proteins in Physiological Fluids.** Rokuro Nakaseko (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 93—112).—A preliminary account is given of an acidimetric method for estimating proteins by precipitating with picric acid in the presence of hydrochloric acid, a given diminution of acidity after precipitation corresponding with a given amount of protein. A modification of Esbach's method is also described in which the precipitation by picric acid is carried out in the presence of $N/20$-hydrochloric acid instead of citric acid. A modification of Roberts and Stolnikov's application of the Heller test is also described. S. B. S.

**Hydrolysis of Proteins in the Presence of Extraneous Materials and the Origin and Nature of the "Humin" of a Protein Hydrolysate.** Ross Aiken Gortner (*Science*, 1918, (N.S.), **48**, 122—124. Compare A., 1916, i, 681; Hart and Sure, A., 1917, ii, 111).—The author points out that the results obtained by McHargue (this vol., ii, 280) are incorrect, because he has failed to recognise that the insoluble residue obtained on digestion of caseinogen is humin, and consequently he has omitted to take into account the nitrogen in this fraction when calculating the distribution of nitrogen in the protein. Hence the general conclusion is that an accurate estimate of the distribution of nitrogen in a feeding stuff cannot be obtained by a direct application of the Van Slyke method of analysis, even when the duration of the hydrolysis is limited to twelve to fifteen hours. H. W. B.

**Acetic-Sulphuric Acid Test for Albumin.** R. Leone (*Policlinico*, 1918, **25**, 224; from *Physiol. Abstr.*, 1918, **3**, 223).—The test depends on the precipitation of protein by a reagent prepared by adding 100 drops of glacial acetic acid and 100 drops of a 25% solution of sulphuric acid to 100 c.c. of a 10% solution of potassium dichromate. S. B. S.

**Protein-Sugar, its Estimation.** H. Bierry and (Mme.) L. Randoin-Vanard (*Soc. Biol.*, May, 1918; from *J. Pharm. Chim.*, 1918, [vii], **18**, 54).—The following method is suggested for the hydrolysis of the protein-sugar compound found in blood. Fifty c.c. of the blood are mixed with 50 c.c. of 0·2% sodium chloride solution, diluted with 90 c.c. of water, and 4 c.c. of sulphuric acid mixed previously with 10 c.c. of water are added; the mixture is then heated in an autoclave at 120° for forty minutes. W. P. S.

# General and Physical Chemistry.

**Spark and Arc Spectra of Gallium, Indium, and Zinc.** L. M. DENNIS and J. ALLINGTON BRIDGMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 1531—1561).—See this vol., ii, 456.

**Absorption Spectra of the Blue Solutions of certain Alkali and Alkaline Earth Metals in Liquid Ammonia and in Methylamine.** G. E. GIBSON and W. L. ARGO (*J. Amer. Chem. Soc.*, 1918, **40**, 1327—1361. Compare *Physical Rev.*, [N.S.], 1916, **7**, 33).—In a previous paper (*loc. cit.*), it was shown that dilute solutions of sodium and magnesium in liquid ammonia had identical absorption spectra. The similarity was explained as due to the dissociation of the metal atoms into electrons partly combined with the solvent, and into cations which are also present in liquid ammonia solutions of salts of the metal. The present paper contains an account of further work on the same subject. The absorption spectra of solutions of lithium, potassium, and calcium in liquid ammonia, and of lithium, sodium, potassium, cæsium, and calcium in methylamine, have been measured. With the possible exception of calcium, the solutions in liquid ammonia have the same absorption spectra as those previously measured. In methylamine, the absorption spectra are entirely different from those in liquid ammonia, a marked absorption maximum appearing which is absent in liquid ammonia solutions. The maximum lies at 650 $\mu\mu$, and is independent of the nature of the metal. In liquid ammonia, the absorption index is independent of temperature, but in methylamine a marked negative temperature coefficient is observed in every case examined, the absorption index diminishing approximately 1% for a rise of 1°. In liquid ammonia, the absorption index is proportional to the total concentration of the metal. In methylamine, the same is true at the position of the band maximum, but at shorter wave-lengths deviations are observed, the absorption increasing more rapidly than Beer's law demands with increase in the concentration. The ratio of the absorption index at 650 $\mu\mu$ to that at 530 $\mu\mu$ increases not only with increasing concentration of the metal, but also with increasing concentration of the reaction product of the metal with methylamine, and probably also with increasing temperature. The experimental results are explained by the following hypothesis. The colour in all cases is due to electrons combined with the solvent. In ammonia, the dissociation of the metal into electrons is nearly complete, and the concentration of electrons uncombined with solvent is negligible compared with that of the solvate electrons. In methylamine, the concentration of un-ionised metal is no longer negligible, and is responsible for the increased absorption at the shorter wave-lengths; further, the solvation of the electrons in methylamine is incomplete and diminishes as the temperature is increased. J. F. S.

**Determination of the Constitution of Coloured Substances from their Absorption Spectra.** F. KEHRMANN and MAURICE SANDOZ (*Helv. Chim. Acta*, 1918, **1**, 270—277).—A résumé of work previously published on the relationships between colour and constitution. J. F. S.

**Absorption of Light and Size of Particles in Disperse Systems.** NILS. E. PIHLBLAD (*Inaug. Diss.*, Upsala, 1918, pp. 85; from *Chem. Zentr.*, 1918, ii, 92—93).—Mainly an account of work which has been published previously (A., 1909, ii, 277, 561, 723; 1910, ii, 946; 1913, ii, 2; 1917, ii, 557). Spectrophotometric observations of a silver hydrosol with very small particles show that the absorption increases towards the region of shorter wave-length, and that the maximum is not attained at $\lambda=400\,\mu\mu$; with larger particles, the maximum lies in the blue-green and passes finally into the yellow region. All the silver hydrosols investigated have a second, better marked maximum in the ultra-violet.

A colloidal solution of Butter-yellow O was obtained by adding water to an alcoholic solution of the dye, the size of the particles being controlled by varying the concentration of the alcoholic solution. As the size of the particles decreases, the absorption approximates to that of a molecular solution. H. W.

**The Stratification of Liquid Layers.** JEAN PERRIN (*Ann. Physique*, 1918, [ix], **10**, 160—184).—A repetition and extension of Johonnott's work (compare *Phil. Mag.*, 1906, 751) on the "black spots" in the films of soap bubbles. The author shows that the number of these coloured regions of uniform thickness may become very great after the addition of colouring matters, such as uranin or æsculin, the soap films assuming a stratified structure. Light favours the evolution of the film, the particular portion of the spectrum which is most active being that which is absorbed by the colouring material in the film. Similarly, rise in temperature favours the stratification. Stratification can also be observed in the films from "soapy" water obtained with rosin. The author suggests a method for enumerating these coloured areas, and shows that their number is independent of the substances added to the water (soap or rosin). In a stratified liquid film, the thickness of each area is a whole multiple of an elementary thickness of about 5 millimicrons. W. G.

**Fluorescence.** JEAN PERRIN (*Ann. Physique*, 1918, [ix], **10**, 133—159).—A theoretical discussion of the subject. The emission of fluorescence implies the destruction of the fluorescent substance, and it is probably only at this moment of destruction that the molecules are fluorescent. Variations of temperature and viscosity do not exert any marked influence on the fluorescence of organic substances. This molecular fluorescence resembles in character the atomic fluorescence or phosphorescence excited by the cathode rays, X-rays, or α-, β-, and γ-rays in inorganic substances. The optimum concentration giving the maximum fluorescence depends on the thickness of the liquid layer studied, but is in all cases less than 20%. Beyond a certain dilution, the fluorescence of a given mass remains constant, the fluorescent power thus having a well-defined limiting value. Each transformation of a fluorogen molecule causes the emission of a quantity of light independent of the exciting illumination and of the concentration, and a formula is given for the calculation of the energy radiated by fluorescence. W. G.

**Crystalloluminescence.** HARRY B. WEISER (*J. Physical Chem.*, 1918, **22**, 480—509).—After an historical survey of the work done on this subject, the author describes a series of experiments on sodium chloride, potassium chloride, potassium bromide, potassium iodide, sodium bromide, and sodium iodide. The effects are produced by precipitating the salts in question by means of alcohol, and in the case of all but sodium iodide with the corresponding halogen acid of various concentrations. The effect of modifying the conditions, by stirring during precipitation, varying the temperature, and increasing the viscosity of the solution by the addition of a colloid (gelatin) and by the addition of a non-electrolyte (sucrose), is also studied. It is shown that crystalloluminescence is caused by chemical action. It is also probable that all cases of triboluminescence are due to chemical action. The luminescent reaction is probably identically the same in the case of substances that show both crystalloluminescence and triboluminescence; the only difference is in the actual way in which the reaction is brought about. The specific reaction which produces crystalloluminescence of the alkali haloids is the recombination of the ions with the formation of non-dissociated salt. In the salts mentioned above, crystalloluminescence was observed in every case save those of sodium bromide and iodide, and in every case the conditions were determined for obtaining the maximum effect. The maximum intensity of the crystalloluminescence results under conditions which favour the accumulation throughout the solution of the largest possible concentration of ions in excess of the equilibrium concentration of ions and allow the luminescent reaction, once started, to go rapidly to completion. The actual conditions differ with different salts. The crystalloluminescence of sodium chloride is bluish-white in colour, and not white as stated by Bandrowski (A., 1895, ii, 66). The colour of the luminescence produced when sodium is burned slowly in air is similar to, but slightly bluer than, the crystalloluminescence of sodium chloride. The difference is due to the specific effect of the anion. J. F. S.

**Some Properties of the Active Deposit of Radium.** S. RATNER (*Phil. Mag.*, 1918, [vi], **36**, 397—405).—The phenomenon of the spreading of the active deposit of radium after deposition on a disk, as though the deposit was slightly volatile, has been investigated, and some remarkable results have been obtained, without disclosing the nature of the phenomenon, but revealing a grave source of error in certain investigations. A disk was mounted in air opposite the plate coated with the active deposit and charged to a high potential, positively to the plate, to prevent recoil phenomena when radium-*A* was present. It always acquired some of the same active deposit as that on the plate. Washing or slightly heating the plate reduces the loss of active deposit from it enormously. When the plate is only exposed to the emanation for a short time, in order to coat it with the active deposit, the proportion of active deposit it loses is much increased. A plate exposed to the emanation for a fraction of a second loses as much radium-*A* as if exposed for several minutes, and for these very short exposures, the amount of radium-*A* lost is comparable with the amount of radium-*B* lost by recoil. For radium-*B*+-*C*, from 0·1 to 0·04% is given up, sufficient except in special circumstances to mask the recoil of radium-$C_2$.

In certain cases, the time in which the quantity of active matter reaching the disk per unit of time falls to half-value was found. For radium-*A* the results were most regular, the time always being 1·4 minutes. If the quantity lost were proportional to the quantity of active matter present on the disk, this time should, of course, have been three minutes. Exposing the active deposit to a violent stream of gas from a cylinder at 80 atmospheres did not reduce appreciably the subsequent loss of active matter, and the physical and chemical conditions of the surface on which the active deposit had been formed had no influence. F. S.

**The Measurement of the Radium Emanation in the Atmosphere.** JOSEF OLUJIĆ (*Jahrb. Radioaktiv. Elektronik.*, 1918, **15**, 158—193).—A simplified method of determining the amount of radium emanation in the atmosphere by condensation with liquid air is described, and the results of measurements extending over several years, both by absorption and condensation methods, given. A connexion has been traced in Freiburg (Switzerland) between the amount of the radium emanation in the atmosphere and the meteorological conditions. The mean emanation content was found to be $131 \times 10^{-18}$ curie per c.c. With a maximum of 305 and minimum of 54, results somewhat higher than these have been found by numerous other investigators in various localities. F. S.

**The Radium Content of Water from the China Sea.** J. R. WRIGHT and G. W. HEISE (*Philippine J. Sci.*, 1918, **13**, [*A*], 49—56).—Tests on a single large sample of sea-water, collected from a depth of 2 metres in the open sea, 8 kilometres from the entrance to Manila Bay, were made by the Chauval absorption method comparatively against a standard radium solution. The mean of these determinations gave the value as only $0·2 \times 10^{-12}$ gram of radium per litre, whereas a test by Joly's direct method gave a value only one-half of this. These values are much lower than those found by other investigators for sea-water from other localities. F. S.

**Radioactivity of Italian Minerals.** L. FRANCESCONI, N. GRANATA, A. NIEDDU, and G. ANGELINO (*Gazzetta*, 1918, **48**, i, 112—113).—Of a number of Italian minerals from different localities, the following are found to be radioactive: pyromorphite, the radioactivity of which varies with the physical characters, especially with the colour; wulfenite and chrysocolla. Certain minerals of lead are found to retard the discharge of the electroscope. Radioactivity has also been observed with malachite from Carrisal (Chile) and with galena (with litharge) from Biokaha (Argentine).
T. H. P.

**Knowledge and Interpretation of Isotopic Varieties of Lead.** K. FAJANS (*Zeitsch. Elektrochem.*, 1918, **24**, 163—169).—In conjunction with A. Nadai and F. Richter, lead was separated from a Norwegian thorite from Langesundfiord, analysing 30·1% thorium, 0·45% uranium, and 0·35% lead, in which the thorium to uranium ratio is 75, and for which the atomic weight of lead, if derived wholly from the uranium and thorium, should be between 207·97 and 208·00. The atomic weight of this lead was found by O. Hönigschmid to be 207·90±0·013, which is the highest value yet experimentally found, that prepared from Ceylon thorite, with the thorium to uranium ratio 55, by Soddy, having the atomic weight 207·77. The small difference between the experimental and calculated values, if significant and due to the thorium lead not being completely stable, shows that the half-period of the thorium lead must be *at least* $1\cdot7 \times 10^8$ years.

The question is discussed whether, in the various kinds of lead having atomic weights between 206 and 208, there are other isotopes than those derived from uranium and thorium, and especially whether common lead, with atomic weight 207·2, is a mixture of these isotopes or a third distinct isotope. If uranium minerals of the same geological age are compared, the ratio $^{206\cdot0}\text{Pb}/\text{U}$ should be constant, and if the variation of the atomic weight of the lead above the value 206·0 is due to the admixture of common lead $\left(^{207\cdot2}\text{Pb}\right)$, the $\beta$-activity of the lead, which is due to Ra-$D$+-$E$, and which is a measure of the $^{206\cdot0}\text{Pb}/\text{U}$ ratio, should decrease as the atomic weight of the lead increases. Three specimens of lead from Joachimsthal pitchblende, the atomic weights of which were I 206·405, II 206·61, III 206·73, were found to possess $\beta$-activity, calculated back to the time of the separation of the lead from the mineral, in the ratio 1:0·639:0·55. It is shown that these figures are in fair agreement with the view that the lead is a mixture of the uranium isotope with common lead, and there are no grounds for assuming the existence of more than three isotopes, uranium lead 206·0, thorium lead 208·0, and common lead 207·2. F. S.

**The Refractive Index and Solubilities of the Nitrates of Lead Isotopes.** THEODORE W. RICHARDS and WALTER C. SCHUMB (*J. Amer. Chem. Soc.*, 1918, **40**, 1403—1409).—The nitrates of lead chosen were (1) from "test-lead" free from silver and tin, and (2) from pure Australian uranio-lead nitrate (compare Richards and Hall, A., 1917, ii, 230) containing lead of atomic weight 206·42. The refractive indices, determined by means of the Abbe crystal refractometer, using a solution of sulphur in methylene iodide of refractive index 1·79 as the medium between the face of the crystal and that of the glass prism of the refractometer, proved to be $n_D = 1·7814$ for each at about 20°, no systematic difference between the individual measurements being detected. The solubilities were determined at 25·02°, after twenty-four hours' shaking in the thermostat, by weighing the filtered solution, then evaporating with sulphuric acid, and heating the lead sulphate to constant weight at 350°. The following table gives the results:

| | Common lead. | Uranio-lead. | Difference. per cent. |
|---|---|---|---|
| Grams $Pb(NO_3)_2$ per 100 grams solution | 37·342 | 37·280 | — |
| Grams $Pb(NO_3)_2$ per 100 grams water | 59·597 | 59·439 | 0·26 |
| Grams Pb per 100 grams water ........ | 37·281 | 37·130 | 0·41 |
| Molal solubility per 1000 grams water | 1·7993 | 1·7991 | — |

Thus no difference has been found in the refractive indices and molal solubilities, showing that, as in other cases, the weight or mass of the two kinds of lead studied is their prime distinguishing feature.

F. S.

**The Ratio of Mesothorium to Thorium.** HERBERT N. McCOY and LAWRENCE M. HENDERSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1316—1326).—The convention applies throughout that "1 mg. of mesothorium" is the quantity of mesothorium-1 + -2 in equilibrium which has a γ-ray activity equal to that of 1 mg. of radium in equilibrium with its first four products. It further appears that the γ-activity was measured through 2·03 mm. of lead + 1·32 mm. of brass. The result of the research was that "1 mg. of mesothorium" is in equilibrium with 19 kilograms of thorium in minerals, or 1 gram of thorium is in equilibrium with $0·524 \times 10^{-4}$ "mg. of mesothorium." It is important to note that the last ratio is only one-sixth as great as the ratio of radium to uranium, namely, $3·23 \times 10^{-4}$ mg. of radium for 1 gram of uranium.

The total γ-activity of thorianite due to thorium, correcting for the absorption of the rays in the mineral and deducting that due to the contained radium, was found to be equal to that of 1 mg. of radium for 6·85 kilograms of thorium, in agreement with a former result by Eve, which indicates that 36·3% of the total γ-activity of thorium is due to mesothorium and the remaining 63·7% to thorium-*D*.

The method followed, since it was not possible to separate sufficient of the minerals to determine the γ-rays of mesothorium directly, was to determine the $\beta$-activity of the mesothorium in arbitrary units, and then the ratio of the $\beta$-activity in these units to the $\gamma$-activity in terms of that of a standard radium preparation, for a specimen of pure mesothorium.

The results for various minerals and various methods of separating the mesothorium varied between $0{\cdot}484$ and $0{\cdot}559 \times 10^{-4}$ for the ratio in question, the mean value $0{\cdot}524 \times 10^{-4}$ being taken, as already given. F. S.

**The Electrical Conductivity of Acids and Bases in Aqueous Solutions.** JNANENDRA CHANDRA GHOSH (T., 1918, **113**, 790—799).—The equation which the author has previously developed (compare this vol., ii, 215, 348), showing the relation between equivalent conductivity and dilution, does not hold in the case of aqueous solutions of strong acids and strong bases, whereas it is found to be valid, for strong acids, in alcoholic solutions. It is well known that in aqueous solution the hydrogen and hydroxyl ions possess abnormally large mobilities, and in explanation of this the author assumes that the electricity is partly carried by the ordinary process of convection and partly propagated through water molecules undergoing alternate dissociation and recombination. On this assumption, it would follow that the real ionic mobilities of hydrogen and hydroxyl ions are less than those usually calculated from experimental data. Assuming that in the case of an aqueous solution of hydrochloric acid, for example, the observed ratio of $\mu_v/\mu_\infty$ is not a real expression for the activity coefficient, it is deduced that the real mobility of the hydrogen ion, $U_{H^{\cdot}}$, is given by the equation $U_{H^{\cdot}} = \{\mu_\infty - \mu_v - (1-\alpha)U_{Cl'}\}/(1-\alpha)$, where $\alpha$ is the activity coefficient and $\mu_\infty$ is given by the expression $\mu_\infty = U_{H^{\cdot}} + U_{Cl'} + C_1$, $C_1$ being a constant independent of the dilution and expressing the conductivity due to the alternating dissociation and recombination of the water molecules and constituent ions. The experimental data on the conductivity of acids must always yield the same values of $C_1$ and $U_{H^{\cdot}}$, as calculated from the above equations, and this is shown to be the case for aqueous solutions of hydrochloric and nitric acids, the values being respectively $197{\cdot}8$ and $152{\cdot}4$ for the former acid and $198{\cdot}8$ and $151{\cdot}3$ for the latter. In a similar manner, the value for $U_{OH'}$ is found to be 109 in the case of potassium hydroxide, $C_1$ being 66. Using these values, $\mu_v$ can be calculated for any dilution, and it is shown that the agreement between calculated and observed values is very close for aqueous solutions of hydrochloric, nitric, naphthalene-$\beta$-sulphonic and toluene-$p$-sulphonic acids, and for potassium hydroxide.

Based on the consideration that only free ions, that is, ions which by virtue of their kinetic energy can overcome the force of electrostatic attraction, have the capacity of regenerating undissociated molecules, a modified Ostwald equation, $(\alpha x)^2/(1-x)V = K$, is developed for weaker electrolytes where the degree of dissociation is less than one; *x* is the fraction of a gram-molecule of acid which has undergone dissociation into ions, and *α* is the activity coefficient at the ionic concentration *x*/*V*. This equation becomes identical with Ostwald's dilution law for very weak electrolytes, where *α* is always very nearly equal to one, and it is shown that it gives very concordant values for the equilibrium constant in the case of "transition" electrolytes, such as cyanoacetic, *o*-nitrobenzoic, dichloroacetic, and trichlorobutyric acids, where Ostwald's equation is not applicable. T. S. P.

**Planck's Formula for the Potential Difference between Solutions and the Values of certain Important Cells.** H. A. FALES and W. C. VOSBURGH (*J. Amer. Chem. Soc.*, 1918, **40**, 1291—1316).—The Planck formula by which contact potentials may be calculated has been examined and tested against the measured contact potentials obtained by the authors according to a new plan, which is based on the absence of a contact potential between solutions of potassium chloride. It is shown that this formula does not represent fact for the liquid junctions *xM*KCl—1·0*M*HCl and *xM*KCl—0·1*M*HCl, where *x* ranges from 0·1—4·1. It is further shown that at 25° no contact potential exists between a saturated solution of potassium chloride (4·1*M*) and hydrochloric acid solutions ranging in concentration from 0·1*M*—1·0*M*. In an *E.M.F.* combination having a contact potential as one of its component *E.M.F.*'s, the diffusion across the liquid junction of the one liquid into the other brings about a decrease in the magnitude of the contact potential, and this decrease may amount to as much as one-tenth of the initial magnitude of the contact potential. For this reason, combinations having only very small or zero contact potentials should be used for precise measurements. As the result of the measurement of some thirty combinations at 25°, the following values are given for the important half-elements, and an accuracy of ±0·0002 volt is claimed: Hg | HgCl | 1·0*M*KCl || 0·5648 volt, Hg | HgCl | 1·0*M*HCl || 0·5567 volt, Pt | $H_2$(1 atm.) | 1·0*M*HCl || 0·2777 volt, Hg | HgCl | 0·1*M*KCl || 0·6168 volt, Hg | HgCl | 0·1*M*HCl || 0·6168 volt, and Pt | $H_2$(1 atm.) | 0·1*M*HCl || 0·2179 volt. A new form of vessel in which to make calomel electrodes is described. This has the advantage that the liquid may be drawn off and replaced without disturbing either the mercury or the electrode. J. F. S.

**Occlusion of Hydrogen and Oxygen by Metal Electrodes.** EARLE A. HARDING and DONALD P. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 1508—1531).—A continuation of work previously published (Smith and Martin, A., 1917, ii, 64) on the change of resistance of platinum wires brought about by the occlusion of hydrogen. In the present paper, the effects on resistance by the occlusion of oxygen and hydrogen in platinum, palladium, iron, and tantalum wires have been studied, together with dimensional changes of the wires. The results confirm the conclusions put forward in the earlier paper. This conception is that hydrogen, when evolved electrolytically, enters the metal of the electrode in a transitional form in the cases in which the gas is largely occluded, and then passes gradually into another form which has the opposite effect on the resistance. Indications have been obtained that the behaviour of oxygen is similar to that of hydrogen. The quantity of the transitional form present when continued electrolysis has led to a steady state of resistance is dependent on the current density. In the case of hydrogen, it may reach very high values, and the consequent diminution of electrical resistance is also large in the case of hydrogen, but much smaller in that of oxygen when the current densities are the same. The transitional form of hydrogen appears to be responsible for the major part of the change of dimensions produced in palladium by electrolytic occlusion. In the more persistent, or "alloy form," the hydrogen is firmly held by palladium up to a critical temperature, which has not been determined, but which probably lies not far from 300°. At this temperature, hydrogen begins to be evolved freely.

J. F. S.

**The Replacement of Platinum in Apparatus for Electrolysis.** PAUL NICOLARDOT and JEAN BOUDET (*Bull. Soc. chim.*, 1918, [iv], **23**, 387—391).—Alloys of gold and platinum containing from 12·5—25% of platinum were examined as to their suitability for use as electrodes under varying conditions, but it was found that they varied too much in weight during electrolysis in alkaline solution or in the presence of sulphides and sodium cyanide. The authors recommend the use of an alloy of gold, silver, and copper in the proportions 920:50:30, and coating the electrodes with a thin layer of platinum (0·005 gram per cm.$^2$). W. G.

**Electrolytic Potential of Alloys. Antimony-Bismuth, Lead-Thallium, Thallium-Antimony.** E. BEKIER (*Chemik Polski*, 1917, **15**, 119—131; from *Chem. Zentr.*, 1918, i, 1000—1001).—The measurement of the electrode potential was effected according to Poggendorf's compensation method. The cells used were of the H-form; in one limb was placed the electrode under investigation, in the other an electrode of the less noble metal. Solutions of salts of the less noble metal were employed as electrolytes.

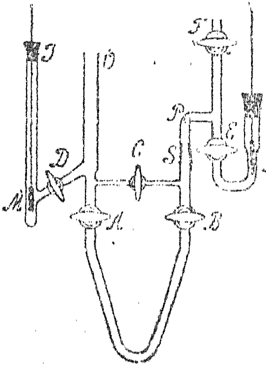
*System Bismuth-Antimony.*—The electrolyte consisted of a saturated solution of potassium antimonyl tartrate. The results show the existence of a continuous series of mixed crystals.

*System Thallium-Lead.*—Electrolyte, thallous chloride solution. Mixed crystals are shown to be present. The region is, however, greater than that indicated by thermal analysis, and extends from 100 to 12% of lead; between 0 and 12% of lead, mixed crystals do not exist.

*System Thallium-Antimony.*—Electrolyte, thallous chloride.

Equilibrium between electrode and electrolyte is rapidly attained except in the case of electrodes with high antimony content. Alloys containing 0—16·4% of antimony show the potential of thallium, and therefore contain the free element; alloys corresponding with the formulæ $SbTl_4$ and $SbTl_3$ also contain free thallium. Alloys containing between 16·49 and 90% of antimony show a constant potential, and thus contain a compound of the two elements. Alloys containing 90% or more of antimony show a rapid decline in potential, which points to the existence of mixed crystals of the compound and antimony. H. W.

**Measurement of the Velocity of Electro-osmosis.** S. Glixelli (*Chemik Polski*, 1917, **15**, 111—118; from *Chem. Zentr.*, 1918, i, 1107—1108. Compare Perrin, A., 1904, ii, 8).—The apparatus (see Fig.) consists of two parts connected by a ground joint, *S*. The diaphragm, which can be gelatinous or pulverulent, is placed in the tube between *A* and *B*. Experiments have shown that a diaphragm of moderately dilute silica gel can withstand slight hydrostatic pressure, so that a cotton-wool support is unnecessary. A large number of substances may be used as diaphragm with the exception of certain sensitive gels, and of such as are in a condition of peptisation. The portions of the apparatus between *A* and *D* and *B* and *E*, which connect the diaphragm with the electrodes, the open tube *O*, and the capillary tube with stopcock *C*, are filled with the substance under investigation. The electrode vessels, *DJ* and *EK*, are completely filled with copper sulphate solution, into which the copper electrodes *M* and *N* dip. The current is sent through the non-polarisable electrode. The tube is filled through *F*. When the electrode vessels have been filled, the diaphragm, which has been repeatedly washed with the electrolyte under investigation, is introduced into *AB*. The solution under investigation is added through *O* and *C*. A capillary tube, *P*, serves to measure the volume of the liquid carried forward by the current. As soon as the liquid has attained equilibrium in *O* and in the measuring tube, *C* is closed and *A*, *B*, *D*, and *E* are opened; the apparatus is then ready for use. Electro-osmosis also occurs through the closed cock *C*, but to an extent which may be neglected. H. W.



**Significance of the Magnetic Susceptibility of Solutions. Nuclear State of Solutions. I.** A. Quartaroli (*Gazzetta*, 1918, **48**, i, 79—101).—Further evidence is advanced (compare A., 1916, ii, 413) confirmatory of the view that support for Weiss's magneton theory cannot be obtained from data regarding dissolved salts. By means of the differential method devised for the estimation of magnetic salts in solution (this vol., ii, 458), and making use of a solution of nickel chloride, carefully freed from cobalt, as standard solution, the author has measured the magnetic susceptibilities of various ferric, ferrous, manganese, cobalt, chromium, and copper salts at different dilutions. The results show that, on the assumption that that of nickel chloride remains constant, in general the molecular susceptibility decreases slowly with increase of the dilution; it is, however, impossible by extrapolation to calculate a limit, since the diminution appears to become rather more rapid as dilution progresses. This holds true even, as is probably the case, if the molecular susceptibility of nickel chloride itself undergoes some diminution on dilution.

The differential method referred to also allows of the alteration of the susceptibility by centrifugation being detected in solutions containing 1 part of ferric or manganese chloride or sulphate in 5000 parts of water, or 1 part of nickel chloride or sulphate per 1000 parts of water.

From the results obtained, the conclusion is drawn that there exists a discontinuity in the relation connecting the variation in concentration with the force tending to oppose such variation, an almost infinitesimal change of concentration counterbalancing appreciable definite forces acting to increase the change. It is suggested that the state of solution represents a special "nuclear" condition, in which, although the characteristic external attributes of liquids are not lost, attractions emanating from the centre of the nuclei (molecules of solute) determine regions of greater rigidity.

The explanation of various phenomena by means of this hypothesis is discussed. T. H. P.

**Atomic Heat, Volume Elasticity, and Characteristic Frequency of Monatomic Metals.** A. L. Bernoulli (*Helv. Chim. Acta*, 1918, 1, 278—288).—A theoretical paper in which it is shown that, on the assumption that the atoms or molecules are solid bodies which under the action of distant repulsive forces set up characteristic vibrations, Magdeburg and others were able to evolve a quantitative relationship between the vibration number and the elastic cubic compressibility, whilst, in opposition to this, the Einstein equation shows that the work of compression only increases the kinetic energy of rotation of the molecule, that is, it does not work against the repulsive molecular distant action. Without any further assumption, this leads to a new proportionality factor from this equation which gives a much better agreement between the value of the ultra-red characteristic vibration obtained from the compressibility and that obtained from the specific heat, always assuming that the material is perfectly elastic. It is also shown that the compressibility may be calculated from the values of the vibration numbers, and that for the metals copper, aluminium, and lead the divergence from Dulong and Petit's law may be calculated from compressibility measurements at stated temperatures. J. F. S.

**The Solid State.** UGO PRATOLONGO (*Gazzetta*, 1918, **48**, i, 193—237).—If a solid is regarded as a congeries of atomic systems which are in static equilibrium and in which the distribution of energy follows the laws defined by the doctrine of Gibbs, the author shows that it is possible to give a satisfactory representation of the solid and of its characteristic properties. The latter are divided into two groups: (1) Those which vary as a function of the modulus of energetic distribution $\theta$ in accordance with the relation $\omega = e^{(\psi-\epsilon)/\theta+\text{const.}}$ where $\omega$ indicates one of the properties of the group and $\psi$ is the mean energy of the systems constituting the whole; this group comprises the specific heat, thermal conductivity, expansibility, and magnetic susceptibility. (2) The thermal radiation, electrical conductivity, and magnetic induction, which are connected with variations of $\theta$ by a relation expressed rigorously by Planck's formula, $\tau = (e^{(\psi-\epsilon)/\theta}-1)^{-1}$, or approximately by Rayleigh's formula, $\tau = \theta e^{(\psi-\epsilon)/\theta} + \text{const.}$, where $\tau$ represents one of the properties of the group.

The relation between the modulus of distribution $\theta$ and the temperature $T$ or the magnetic field $H$ is, for each of the properties considered, one of simple equality. In the phenomena of thermal radiation, electrical and thermal conductivity, and magnetic susceptibility, the relation $\theta = T$ is found. In the case of specific heats, the relation has the form $\theta = T^{\gamma}$, whilst with magnetic induction it is expressed by $\theta = H$ or $\theta = H^2$, according as the induction is due to fields of high or low intensity. The reasons of such multiplicity of relations lies evidently in the intimate mechanism of the energy exchanges between the atomic systems, but are as yet unknown.

In each of the phenomena of the first group, considered separately, there participate only those atomic systems the energy of which has reached a critical value $\epsilon$; the latter is different for the different physical phenomena and characteristic for every atomic or molecular species, being connected with the atomic frequency according to a general relation. Between the limits of approximation of the methods of investigation, the difference between the mean atomic energy and the critical energy, $(\psi - \epsilon)$, which may be termed the relative critical energy, appears to be proportional to the atomic frequency.

As far as the available experimental data go, the curves representing the specific heats as a function of the temperature seem to be grouped in two distinct types; the fundamental difference thus indicated is apparently related to the crystalline form.

The phenomena of the second group are functions of the energy content of the whole system considered. T. H. P.

**Still for the Continuous Preparation in Quantity of Water of High Purity.** HAL W. MOSELEY and ROLLIN G. MYERS (*J. Amer. Chem. Soc.*, 1918, **40**, 1409—1411).—The apparatus consists of two 5-litre, round-bottomed Pyrex glass flasks which are set at an angle of 60°. The first flask is fitted with a pressure tube, a supply tube, by means of which ordinary distilled water is admitted, and an exit tube which leads to the bottom of the second flask. The second flask is fitted with a steam delivery tube and an exit tube which carries a trap. The exit tube of the second flask is connected to a Findlay adapter, which in its turn is attached to a tin condenser. The water in the first flask contains 10% of potassium dichromate and 5% of sulphuric acid, whilst that in the second flask contains barium hydroxide. Both flasks are heated, and the apparatus is capable of furnishing continuously about a litre of very pure water in an hour. The stoppers used in the flasks are made of Portland cement, whereby the use of rubber and cork is rendered unnecessary. J. F. S.

**The System: Acetone-Ethyl Ether.** JITSUSABURO SAMESHIMA. (*J. Amer. Chem. Soc.*, 1918, **40**, 1482—1503).—The author has determined the vapour density of ethyl ether and acetone by a slightly modified form of Menzies' method at 25°, and finds that at this temperature both vapours are non-associated. The densities of mixtures of acetone and ethyl ether have been determined over the whole range of composition 0—1 molecular fractions at 25·04°. Series of vapour pressure determinations of binary mixtures of the same substances and of the simple substances have been determined at 20° and 30°. It is shown that in liquid acetone the reaction $3C_3H_6O \rightleftharpoons (C_3H_6O)_3$ takes place. The vapour pressure of the acetone–ethyl ether system, the heat of vaporisation of acetone, the heat of mixing acetone and ethyl ether, and the volume contraction on mixing were calculated from the experimental data, and the values compared with directly observed results. The agreement is fairly good and affords confirmation of Ikeda's conclusions in connexion with quasi-ideal solutions (A., 1908, ii, 932). J. F. S.

**The System: Benzene-Carbon Disulphide.** JITSUSABURO SAMESHIMA (*J. Amer. Chem. Soc.*, 1918, **40**, 1503—1508).—A series of vapour pressure determinations of mixtures of benzene and carbon disulphide has been carried out at 20°, 25°, and 30°, and the results plotted. From the results, the heat change on mixing and the change of free energy have been calculated for various mixtures at 25°. J. F. S.

**Fractional Distillation Tube.** W. G. FRIEDEMANN (*J. Amer. Chem. Soc.*, 1918, **40**, 1411).—A fractional distillation column can be made by connecting together Kjeldahl trap bulbs by means of rubber tubing. J. F. S.

**Critical Temperature of Mercury.** (MISS) JULIE BENDER (*Physikal. Zeitsch.*, 1918, **19**, 410—414).—In continuation of work previously published (A., 1915, ii, 673), further constants of mercury, are now given. All experiments were carried out in capillaries of quartz. A series of density determinations of liquid and gaseous mercury have been made at a series of temperatures, and the following values obtained: mercury vapour, D 0·7 at 1050°, 1·15 at 1210°, 1·35 at 1230°, 1·65 at 1295°, 1·90 at 1330°, and 2·50 at 1380°. These results imply that the critical temperature is above 1370°, a value considerably higher than that accepted by previous observers. As a first approximation, the value 200 atms. is given as the lower limit of the critical pressure. The density of liquid mercury has been determined at high temperatures, and the following figures obtained: 500°, D 12·38; 600°, D 12·10; 800°, D 11·49; 900°, D 11·11; 1000°, D 10·67; 1100°, D 10·18; 1200° D 9·57; 1300°, D 8·90. The emission of light of mercury has been examined; at 1270° the vapour emits no visible light, whilst the liquid emits a dazzling white light. Above 1270° the vapour space appears to be filled with weak blue light. From determinations of the light emission, it is shown that the temperature of mercury vapour can be fairly accurately determined. The results given in this last section of the paper are of a preliminary nature.

J. F. S.

**Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum.** IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1918, **40**, 1361—1403. Compare A., 1917, ii, 19, 525).—The theory put forward previously (*loc. cit.*) is elaborated and discussed; it is shown that the theory demands that in typical cases of true adsorption the adsorbed film should not exceed one molecule in thickness. This is contrary to the usual view, and the discrepancy is accounted for by the fact that in most cases porous bodies in which the adsorbing surface is indeterminate have been used in the experiments, or saturated vapours have been used, so that condensation of liquid took place in capillary spaces; also solution and absorption have been mistaken for adsorption. The mechanism of adsorption is discussed, and it is shown that the forces causing adsorption are typically chemical and exhibit all the differences in intensity characteristic of chemical forces. The adsorption of the permanent gases by solids involves only secondary valencies, but a great many cases of adsorption by metals are caused by primary valencies. Under certain conditions, stoicheiometric relations should govern the amounts of gases adsorbed on saturated surfaces. These relationships often fail to hold, because of steric hindrance effects between the adsorbed molecules. Equations are developed which give the relation between the amount of adsorbed gas and the pressure and other variables under various conditions. A number of experiments are described in which the amount of adsorption of nitrogen, methane, carbon monoxide, argon, oxygen, carbon dioxide, and hydrogen on surfaces of glass, mica, and platinum has been determined at various temperatures and low pressures (circa 0·1 mm. of mercury). At the ordinary temperature, the adsorption by mica and glass was negligible, less than 1% of the surface being covered by a single layer of molecules. At $-183°$ and $-118°$, relatively large amounts of gases were adsorbed, except in the case of hydrogen, and at higher pressures the surfaces tended to become saturated with the gas. The maximum quantities adsorbed, even with saturated surfaces, were always somewhat less than the amounts expected from a unimolecular layer. The amounts of the different gases adsorbed by saturated surfaces of mica and glass were always in the order: hydrogen, oxygen, argon, nitrogen, carbon monoxide, methane, and carbon dioxide. The amounts adsorbed by mica and glass varied with pressure according to the equation $N/N_0 \times \eta = \theta_1 = \sigma_1\mu/(1+\mu\sigma)$, in which $N$ is the Avogadro constant $6{\cdot}06 \times 10^{23}$ mols. per gram-mol., $\eta$ is the number of gram-molecules of gas absorbed per unit area of surface, $\theta$ is the fraction of the surface actually covered by adsorbed molecules, $\mu$ is the number of molecules striking each cm. of surface per second, $\sigma = \alpha/\nu_1$, where $\alpha$ is the fraction of the molecules which on striking the surface condense, and $\nu_1$ is the rate at which the gas would evaporate if the surface were entirely covered. The adsorption of all the above gases is reversible. The phenomena observed with platinum are quite different. No adsorption of gases could be observed, even at $-183°$, until the platinum had been activated by heating to 300° in a mixture of hydrogen and oxygen at low pressure. After this activation, hydrogen and oxygen, or carbon monoxide and oxygen, reacted together readily at the ordinary temperature in contact with the platinum. The platinum was then found capable of adsorbing oxygen, hydrogen, or carbon monoxide. The maximum quantities of oxygen and carbon monoxide corresponded with unimolecular layers. The oxygen could not be driven off either by heat or by exhaustion. When the platinum was in contact with an excess of oxygen, the amount of oxygen adsorbed increased as the temperature was raised, but was reversible. Adsorbed carbon monoxide could not be removed by exhaustion at the ordinary temperature, but at 300°, part of it could be pumped off. When oxygen was brought into contact with carbon monoxide adsorbed on the platinum, it reacted rapidly to form carbon dioxide, which at the ordinary temperature showed no tendency to be adsorbed. In a similar way, carbon monoxide brought into contact with adsorbed oxygen reacted immediately. These cases of adsorption are clearly due to primary valencies.

J. F. S.

**[Chemical and Physical Theories of the Action of Toxins, Dyes, etc.]** P. Karrer (*Chem. Zeit.*, 1918, **42**, 521—522).—According to the physical theory (compare Traube, A., 1912, ii, 740), a toxin does not combine chemically with the substance (for example, albumin) on which it has an effect, but causes a precipitation or coagulation of the substance. The author is of opinion that the action is purely chemical; in the experiments described by Traube, the minute quantity of precipitant employed was still more than was required to precipitate the substances as chemical compounds. W. P. S.

**Molecular Weights of Salts Dissolved in Urethane.** G. Bruni (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 321—323; *Gazzetta*, 1918, **48**, ii, 39—42).—Criticism of Stuckgold's results (this vol., ii, 99), some of which are erroneous and others inaccurately calculated; the literature of the subject has been disregarded. For potassium iodide in urethane, Stuckgold's cryoscopic measurements gave values of 94 and 97 for the molecular weight, whereas the author finds values varying from 146·6 to 152·1, the mean being 150·2; the degree of dissociation is hence $\alpha = 0{\cdot}10$, and not 0·71—0·76. T. H. P.

**Osmotic Action of Solutions of Sucrose, Silver Nitrate, and Lithium Chloride in Pyridine, when separated from Pyridine by a Rubber Membrane.** Alfred E. Koenig (*J. Physical Chem.*, 1918, **22**, 461—479).—Osmotic pressure determinations have been made of solutions of sucrose, silver nitrate, and lithium chloride in pyridine, using a modified form of cell and a thin sheet of dental rubber as membrane. Solutions of concentrations from $0{\cdot}2N$—$0{\cdot}025N$ were used, and all measurements were made at 25°. The osmotic pressure found for sucrose solutions was very near that demanded by the gas laws, but the values for silver nitrate and lithium chloride were much lower than those of sucrose of equal molecular concentration. It was found that, after having reached a maximum, the osmotic pressure decreased. This seemed to be due to an alteration in the nature of the rubber, due to its contact with pyridine, for membranes used a number of times with fresh solutions did not give as high a pressure as the unused rubber, whilst the same solution used several times with fresh rubber each time gave practically the same pressure in all measurements. This the author takes to be a substantiation of the statement of Kahlenberg, that the osmotic pressure developed by a given solution depends on the nature of the semipermeable membrane. J. F. S.

**Inhibition in the Diffusion of Salts into Colloids.** Tetsutaro Tadokoro (*J. Tokyo Chem. Soc.*, 1918, **39**, 61—73).—It has been observed that the diffusion of a mixed salt solution into a colloid, such as gelatin, egg-white, and the expressed juices of plants, through a semipermeable membrane is opposed by some inhibitory factor. The mixed salt solutions, which can coagulate these colloids, show that they are subjected to a considerable hindrance during diffusion. The cause of this phenomenon is considered to be as follows: a new membrane is formed at the surface of the colloid by the salts after they have diffused through the semipermeable membrane; this new membrane then retards the further diffusion of the salts. J. F. S.

**Ionic Theory of Solid Substances.** A. L. Bernoulli (*Helv. Chim. Acta*, 1918, **1**, 289—296).—A theoretical paper in which it is shown that the ion frequencies of solid substances may be calculated from the volume elasticity, compressibility, and wave-length of the absorption bands at low temperatures.

J. F. S.

**The Development of Crystals.** René Marcelin (*Ann. Physique*, 1918, [ix], **10**, 185—188).—A microscopic study of the crystallisation of *p*-toluidine shows that the crystals develop, not at the base, but at the surface by successive depositions. The layers of material which are deposited maintain a perfectly uniform thickness, which may be as small as three molecular diameters. Similarly, when a crystal dissolves, the change goes on at the surface, the material disappearing by successive layers, each layer maintaining a constant thickness, and it is found that the material has a crystalline structure at a thickness of only twenty molecular diameters.

W. G.

**Theory of Gel Structure.** W. A. Osborne (*Proc. Roy. Soc., Victoria*, 1918, [N.S.], **30**, 153—158; from *Physiol. Abstr.*, 1918, **3**, 308).—The author discusses the question as to whether the more solid phase in a gelatin jelly has a crystalline structure or is truly amorphous, and describes experiments on the shape of bubbles and on fracture, which, without being conclusive, indicate lack of sectorial character. Some experiments on the Struve-Baumstark phenomenon with gelatin gels are also described. This phenomenon concerns the extrusion of water from tissues, soaps, etc., on treatment with ether. A 2% gelatin jelly on immersion in ether extrudes water, but a 5% set jelly does not. The weaker jelly is supposed by the author to hold part of the more liquid phase by capillarity in the lattice of the more solid phase, whereas in the stronger jelly the water exists in solid solution in the substance of the framework.

H. W. B.

**Structure of Gels.** W. Bachmann (*Kolloid Zeitsch.*, 1918, **23**, 85—100).—After a fairly long historical introduction on the structure of gels, the author describes a series of experiments on the vapour pressure isothermals, the ultramicroscopic character, and the capillary radii of the gels of gelatin in alcohol and benzene. It is shown that these gels, apart from minor points, which affect the general character but little, and are based on the mechanical properties, present a far-reaching similarity in respect of the course and hysteresis cycles of their vapour pressure isothermals with the gels of silicic acid and other substances. The isothermals are in all cases built on a common type, which is approximately represented by the silicic acid gel in water. This similarity points to a common cause as the reason for the processes which obviously take place in the same way, namely, lowering of the vapour pressure of the imbibition liquid by the action of capillarity in an amicroscopic capillary system. Such a similarity in behaviour during the filling with liquid and emptying can be foreseen from Zsigmondy's theory for all porous substances with fine capillaries and resisting walls if secondary chemical processes are ruled out. This theory points to the structure of gels being that of a mass interspersed by a large number of fine capillaries. This type of hysteresis cycle must, if the theory is correct, be independent of the inhibition liquid and also of the gel material. These demands are amply confirmed by the experimental results. The application of the capillary theory to hardened gelatin gels allows of an approximate calculation being made of the volume of the capillaries. As a mean, it is shown that they are thirty to one hundred times smaller than the value put forward by Bütschli. It is also shown that capillaries of the size indicated by Bütschli (700—800 $\mu\mu$) can have no effect in the lowering of the vapour pressure. J. F. S.

**Esterification in Aqueous Solution.** ATTILIO PURGOTTI (*Gazzetta*, 1918, **48**, ii, 54—62).—Experiments with alcohol and acetic acid show that in aqueous solution only slight esterification takes place, equilibrium being reached when about 1·2% of acetic acid is converted into the acetate. Sodium chloride increases this proportion to 7% and hydrochloric or sulphuric acid to about 19%. The catalytic effect of both organic and inorganic acids on this reaction is in proportion to their degree of dissociation. Gallic and tannic acids, however, retard the esterification. Phenols also exhibit catalytic action on the reaction, picric acid being the most effective, *m*-, *o*-, and *p*-cresols then following in order. Dihydric phenols are less active catalysts than the monohydric, whilst the trihydric ones behave like gallic and tannic acids. T. H. P.

**Velocity of Hydrolysis of Esters of the Types $OR\cdot[CH_2]_n\cdot CO_2R'$, $OR\cdot[CH_2]_n\cdot O\cdot CO'\cdot R$, etc.** M. H. PALOMAA (*Ann. Acad. Sci. Fennicae*, 1914, [*A*], **5**, No. 4, 1—23; from *Chem. Zentr.*, 1918, i, 1143—1144. Compare A., 1914, i, 136).—In connexion with the earlier investigations on the influence of the position of the oxygen atom in the chain on the velocity of hydrolysis of esters, the author has now determined the velocities of hydrolysis of the same series of substances in alkaline solution at 15°. The reaction appears to be bimolecular, and a table of constants is given in the original.

The velocity constants for alkaline solution are approximately parallel to the dissociation constants of the corresponding acids. A minimum velocity, as in the case of acid hydrolysis, is not observed. The molecular weight has little influence on the constants. H. W.

**Influence of Temperature and Constitution on the Velocity of Hydrolysis of Esters by Hydrogen [Ion] Catalysis.** FRIEDRICH BÜRKI (*Helv. Chim. Acta*, 1918, **1**, 231—250).—A large number of experiments have been carried out on the hydrolysis of esters to ascertain (1) the influence of various acids, (2) the influence of concentration of the acid, (3) the influence of the constitution of the ester, and (4) the influence of temperature on the velocity of hydrolysis. The catalytic action of hydrochloric acid, nitric acid, sulphuric acid, and phosphoric acid of various concentrations on the hydrolysis of ethyl acetate has been determined at 25°, 30°, and 40°. The hydrolysis of the following esters by 0·1*N*-hydrochloric acid at 40° has been quantitatively determined: methyl propionate, methyl *n*-butyrate, methyl $\alpha$-chloropropionate, methyl $\alpha$-dichloropropionate, allyl acetate, methyl crotonate, methyl *iso*crotonate, ethyl malonate, ethyl oxalate, ethyl acetoacetate, and *iso*amyl formate. It is shown that the relative velocity of hydrolysis by means of hydrogen ions is the same for all esters over the range 25—40°. Quantitative measurements could not be carried out in the case of acetoacetic ester, for the free acid undergoes the ketone decomposition at 40°. The catalytic action of the acids examined increases rapidly with increasing temperature. The increase is greatest with hydrochloric acid, somewhat smaller with nitric acid, and least with sulphuric acid. With a given concentration and temperature, the reaction proceeds most rapidly with nitric acid, somewhat less rapidly with hydrochloric acid, and most slowly with sulphuric acid. The influence of the substitution of one chlorine atom in the acid of the ester produced in the only case examined, that of $\alpha$-chloropropionic ester, a lowering in the velocity of hydrolysis of about two-thirds the value of the unsubstituted ester. The introduction of two chlorine atoms brings the value up again to about five-sixths of the original value. The introduction of an unsaturated group into the alcohol produced no effect on the velocity of hydrolysis, whereas an unsaturated group in the acid greatly diminishes the velocity. The velocity constants multiplied by $10^6$ are as follows at 40°: ethyl acetate, 5629; allyl acetate, 4642; methyl propionate, 6138; methyl $\alpha$-chloropropionate, 2194; methyl $\alpha$-dichloropropionate, 5281; methyl butyrate, 3462; methyl crotonate, 221; methyl *iso*crotonate, 985; ethyl malonate, 1158; *iso*amyl formate, 10,408.

J. F. S.

**Dissociation Constants of Normal Acids and Esters of the Oxalic Acid Series. III. Effect of the Substitution of a Methylene Group by Bivalent Atoms and Radicles.** M. H. PALOMAA (*Ann. Acad. Sci. Fennicae*, 1917, [*A*], **10**, No. 16, 1—26; from *Chem. Zentr.*, 1918, i, 1144. Compare A., 1913, i, 8).—Previous investigations have shown that the replacement of a methylene group in organic acids and esters by :O or :CO increases certain affinity constants in the homologous series (electrolytic dissociation constant, velocity of hydrolysis by alkali) and diminishes certain others, and that a minimum occurs with a certain position of the oxygen atom (velocity of hydrolysis by acid, velocity of esterification). The affinity minimum occurs when the oxygen is in the $\beta$-position or in the position 1:4—5. The result is explained by supposing that intramolecular ring formation occurs through the medium of the partial valency of the oxygen. This hypothesis has been tested with the methyl esters of the oxalic acid series, which were dissolved in 50% methyl alcohol and hydrolysed with 0·05 mol. hydrochloric acid at 25°. Since the reaction leads to an equilibrium, the velocity of hydrolysis, as well as that of esterification, was determined. The results are expressed in tables. The minimum occurs with compounds in which the formation of a 5- or 6-membered ring is possible, as is demanded by the hypothesis. H. W.

**Neutral Salt Catalysis. I. Rôle of the Solvent in Neutral Salt Catalysis in Aqueous Solutions.** HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1918, **40**, 1461—1481).—A number of experiments on the accelerating effects of the chlorides of lithium, sodium, and potassium, in varying concentrations, on the iodine ion catalysis of hydrogen peroxide and on the hydrogen ion catalysis of methyl acetate are described. It is shown that the effects of the different salts are roughly proportional to their ionic hydration values as determined by Washburn. This is also shown to be the case in the hydrochloric acid catalysis of acetochloroanilide. In some cases, the effects of different salts on the velocity of hydrolysis of ethyl acetate are not proportional to the ionic hydration values, and reasons have been advanced to explain this abnormality. The chlorine ion activities up to a concentration $3N$ have been determined by measurement of cells of the type $Hg|HgCl|NaCl(0{\cdot}1N)||NaCl(c)|HgCl|Hg$. The relationship $K_1/K_2=a_1/a_2$ holds rigorously, where $K_1$ and $K_2$ are the velocity constants of the decomposition of hydrogen peroxide in the presence of potassium iodide and potassium chloride, and potassium iodide-sodium chloride solutions, respectively, both being of the same normality, and $a_1$ and $a_2$ are the chlorine ion activities of the potassium chloride and sodium chloride respectively. Relationships are expressed between the hydration values of the ions of neutral salts on the reaction velocities in neutral solutions, and also on the activities of salt solutions. J. F. S.

**The Atom Model.** WILH. H. WESTPHAL (*Ber. deut. physikal Ges.*, 1918, **20**, 88—92).—Polemical. In a short theoretical paper the author contests the objections to the Bohr atom model raised by Stark (this vol., ii, 141). J. F. S.

**Elements in Order of their Atomic Weights.** RAYMOND SZYMANOWITZ (*Chem. News*, 1918, **117**, 339—340).—It is found that if the elements are written down in order of their atomic weights, a definite numerical sequence is to be observed in the values of the atomic weights. Thus, if the first element has an atomic weight of $x$, the second will be $x+3$, the third $x+3+1$, the fourth $x+3+1+3$, and so on, adding alternately 3 and 1 to the preceding values. Of the 83 elements, 17 do not fall into this arrangement, whilst there are several gaps with no known element to fill them. It is pointed out that several of the elements which do not conform with the arrangement are little known rare elements, and that until 1918 these elements had atomic weights attributed to them which conformed with the present scheme.

J. F. S.

**Elements in Order of their Atomic Weights.** F. H. LORING (*Chem. News*, 1918, **117**, 352).—The author points out that regularities of the type put forward by Szymanowitz (preceding abstract) have already been indicated, notably by Comstock (A., 1908, ii, 477).

J. F. S.

**Interfacial Tension and Complex Molecules.** G. N. ANTONOFF (*Phil. Mag.*, 1918, [vi], **36**, 377—396).—A theoretical paper in which, from the modern conceptions of atoms and molecules, a theory of molecular attraction has been developed. This theory implies that molecular attraction depends on the same forces as chemical affinity. A relationship between surface tension and molecular pressure has also been deduced. The interfacial tension $\alpha_{12}$ between two liquids is equal to the difference of the surface tensions against air $(\alpha_1-\alpha_2)$ of both superposed liquid layers in equilibrium. This result is in agreement with experimental values. Two superposed liquid layers in equilibrium are to be regarded as solutions in the same solvent, and must contain an equal number of molecules per unit volume. The so-called univariant systems may be obtained without fulfilment of the requirements of the phase rule if the molecules of the added component combine with those in solution without increasing their number.

J. F. S.

**Theobald van Hogelende.** F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 1216—1258).—An account of the life and work of the alchemist Theobald van Hogelande, who was born at Middleburg about 1560, studied at Leyden in 1580, and at Paris in 1581. Most of his life was spent abroad, but he died in 1608, probably at Leyden.

A. J. W.

**Isaac of Holland and Jan Isaac of Holland.** W. P. JORISSEN (*Chem. Weekblad*, 1918, **15**, 1343—1351).—A further contribution to the history of these alchemists (compare A., 1917, ii, 198, 461, 529).

A. J. W.

**Simplification of some well-known Chemical Experiments.** S. GENELIN (*Zeitsch. physikal Chem. Unterr.*, **31**, 91—93; from *Chem. Zentr.*, 1918, ii, 250).—(1) *Reduction of Nitric to Nitrous Acid.*—Nitric acid (D 1·4, 0·5 c.c.) is mixed with water (500 c.c.) in two cylinders; after addition of potassium iodide-starch solution to each, a wad of zinc wool is dipped into one of the solutions. Blue streaks are formed in a few seconds.

(2) *Oxidation of Ammonia to Ammonium Nitrite in the Air.*—Ten c.c. of concentrated ammonia solution are placed in a 2-litre flask, which is shaken for about a minute; the flask is placed horizontally, and a glowing piece of platinum foil is introduced. The platinum continues to glow, and brown fumes of nitrogen peroxide appear, which are replaced by a dense fog of ammonium nitrite. When the fog has subsided, the flask may be filled with water and the presence of the nitrite demonstrated by addition of sulphuric acid followed by potassium iodide and starch. (3) *Oxidation of Sulphur Dioxide to Sulphur Trioxide in Air.*—The experiment is performed in exactly the same manner as that just described, but with the replacement of ammonia by a solution of sulphur dioxide. (4) *Lead has a bright surface when it remains quite free from lead oxide.*—Molten lead is poured into a glass tube, the lower end of which is sealed, whilst the upper end is expanded to form a funnel; the tube is subsequently sealed.

H. W.

**Experiments to Demonstrate the Velocity of Explosion of Mercury Fulminate.** M. Mittag (*Zeitsch. physikal Chem. Unterr.*, **31**, 93—95; from *Chem. Zentr.*, 1918, ii, 250).—About 20—30 mg. of mercury fulminate are placed in an empty percussion cap resting with open end upwards on a piece of foil at least 4 mm. thick; the foil is heated with the full flame of a Teclu burner. Explosion follows in ten to thirty seconds. The approximate duration of the flame can be shown by allowing it to illuminate a disk divided into forty-eight equal sectors, coloured alternately black and white; the disk is kept in rapid rotation (about 1500 revolutions per minute) by a small motor. Since the disk appears stationary, the duration of the explosion must be considerably shorter than 1/1200 second. Repetition with a disk containing ninety-six sectors shows the duration to be somewhat shorter than 1/2400 second.

H. W.

## Inorganic Chemistry.

**Two Sets of Distillation Apparatus for the Preparation of Large Quantities of Chemically Pure Acids in the Laboratory.** E. Krummenacher (*Schweiz. Chem. Zeit.*, 1917, **1**, 116—120; from *Chem. Zentr.*, 1918, ii, 1).—Detailed descriptions are given of apparatus for the preparation of hydrochloric acid on the counter-current principle, and for the distillation of nitric acid in a vacuum.

H. W.

**Reduction in the Strength of Hypochlorite Solutions on Keeping.** I. M. Kolthoff (*Pharm. Weekblad*, 1918, **55**, 1318—1324).—Under the influence of light, hypochlorite solutions decompose rapidly, with formation of chlorate. In absence of light, solutions of moderately strong alkaline reaction keep for two months without much change (compare Bouvet, this vol., ii, 397). A. J. W.

**Limit and Composition of the Terrestrial Atmosphere. Aurora Borealis, Aerolites, and Shooting Stars.** A. Véronnet (*Compt. rend.*, 1918, **167**, 636—638).—A theoretical discussion of the composition of the terrestrial atmosphere at heights varying from 0—300 km. The percentage of nitrogen increases regularly up to 100 km., and at a height of 100—150 km., nitrogen forms 0·96 of the atmosphere at a pressure less than $1 \cdot 10^{-6}$ atmos., this being the region of auroræ boreales. The phenomena of aerolites and shooting stars are also discussed. W. G.

**Simple Method for the Preparation of Phosphorous Acid.** T. Milobendzki and M. Friedman (*Chemik Polski*, 1917, **15**, 76—79; from *Chem. Zentr.*, 1918, i, 993).—Phosphorus trichloride is conveniently prepared by leading a current of chlorine through a layer of boiling phosphorus trichloride which covers a quantity of red phosphorus. The gas should not be introduced until the trichloride actually boils. The product thus obtained is pure and has b. p. 75·5°/749 mm. Formation of phosphorus pentachloride is not observed even after complete consumption of phosphorus. The production may be made continuous by distilling off the phosphorus trichloride and introducing the requisite quantity of phosphorus.

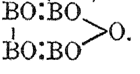
The violent reaction in the preparation of phosphorous acid from phosphorus trichloride may be avoided by effecting the decomposition of the latter with concentrated hydrochloric acid instead of with water; in the first instant, a slight rise in temperature is noted, but reaction proceeds subsequently at the ordinary temperature. Concentrated hydrochloric acid has the further advantage that it forms two layers with phosphorus trichloride, so that only a portion of the latter reacts at any given instant. H. W.

**Behaviour of Phosphates at the Anode.** Fr. Fichter and Jakob Müller (*Helv. Chim. Acta*, 1918, **1**, 297—305).—By the anodic oxidation of a solution of potassium monohydrogen orthophosphate (2*M*) between two platinum electrodes in an undivided cell and in the presence of 2*N*-potassium fluoride and 0·32 gram of potassium chromate per litre, the authors have prepared the potassium salts of monoperphosphoric acid ($K_3PO_5$) and perphosphoric acid ($K_4P_2O_8$). The best yield is obtained at 5° and when working with a current density of 0·01 ampere per sq. cm. These salts have previously been prepared by Schmidlin and Massini (A., 1910, ii, 490), who obtained the acids by the action of concentrated hydrogen peroxide on phosphoric oxide, but failed to obtain the salts by the above method. The properties of the substances obtained are identical with those described by Schmidlin and Massini. J. F. S.

**Preparation of Hypophosphates.** R. G. Van Name and Wilbert J. Huff (*Amer. J. Sci.*, 1918, [iv], **46**, 587—590).—After a recapitulation of the methods available for the production of hypophosphates, the authors describe a method which requires little attention in carrying out. A number of sticks of phosphorus are cast round glass rods, and these are supported from a plaster cover in a stout glass vessel containing about a litre of water and 250 grams of sodium carbonate, which need not be dissolved. The phosphorus sticks used were 9 c.m. long and 1·7 c.m. in diameter, and protruded about 1 c.m. from the solution. The whole is then put in a cool place and left to react. At the end of two or three days, some of the solution is withdrawn and tested with Congo-red to find the end of the reaction, which is reached when the turning point of the Congo-red is obtained. The phosphorus is then removed and placed in a similar solution. The product, sodium hydrogen hypophosphate, is found in part as a crystalline precipitate at the bottom of the jar, whilst the residue is obtained by concentrating the solution. It is crystallised to remove the accompanying phosphates and phosphites. The best temperature to carry out the reaction is 10—15°, and the yield is 10—16% of that theoretically possible.

J. F. S.

**The Compound $H_2B_4O_6$ and its Salts.** Rames Chandra Ray (T., 1918, **113**, 803—808).—It has previously been shown (compare T., 1914, **105**, 2162) that the so-called amorphous boron, prepared by the reduction of boron trioxide by means of magnesium, probably consists of a solid solution of a lower oxide of boron, sometimes in combination with a little magnesium oxide, in elementary boron. The author has now extracted the fusion thus obtained with water, removed the boric acid from the solution by the method of Travers, Ray, and Gupta, and determined the ratios $B/Mg$ and $B_2O_3$/(residue less $MgO$) in the resulting filtrate. The former ratio is found to be very nearly 4 and the latter 1·124, which closely approximates to the value of the ratio $2B_2O_3/B_4O_5$, which is 1·129. It is concluded that the filtrate contains a magnesium borite, the formula of which may be written $MgO,B_4O_5$, and this is confirmed by molecular weight determinations by the freezing-point method. The *potassium* salt, $K_2B_4O_6$, has been isolated by precipitating a solution of the magnesium salt with potassium hydroxide in equivalent proportions, and the formula confirmed by analysis and cryoscopic determinations. The constitutional formula of the corresponding acid is considered to be $BO(OH){:}BO{\cdot}BO{:}BO(OH)$, that of the oxide, $B_4O_5$, being



$$\begin{array}{l} BO{:}BO \\ | \qquad\quad >O \\ BO{:}BO \end{array}$$

T. S. P.

**Silicic Acid Gels.** Harry N. Holmes (*J. Physical Chem.*, 1918, **22**, 510—519).—Methods for preparing silicic acid gels from water-glass by means of phosphoric, citric, acetic, formic, tartaric, sulphuric, hydrochloric, lactic, trichloroacetic, monochloroacetic, and nitric acids are described. The concentrations and quantities of the various acids necessary to produce a gel which will set in a definite time have also been determined. The influence of temperature on the gels has been studied over the range 0—100°. It is shown that gels containing a very slight excess of hydroxyl ions set most rapidly, almost immediately if not too dilute, but with increase of hydrogen ion concentration the time required to set increases rapidly. With each acid there is a definite concentration of hydrogen ion which delays the setting indefinitely. At still higher concentrations of the same acid, the time required again becomes measurable and rapidly decreases to an almost instantaneous setting. Contrary to Flemming (A., 1902, ii, 646), it is shown that, in addition to the concentration of silicic acid, temperature, and catalytic action of the ions, the dehydrating influence of the non-ionised molecules also exerts a marked action on the time required for setting. J. F. S.

**The Dissociation of Salt.** H. V. THOMPSON (*Trans. Ceramic Soc.*, 1918, **17**, (2), 340—350).—Salt was heated for six hours in a platinum tube in a current of dry or moist air at a temperature of 110°, and the amount of salt vaporised and redeposited in a cool part of the tube was weighed. With dry air, the amount of salt volatilised was about 0·055 gram per litre, but with air saturated with moisture it rose to 0·08 gram per litre, an increase of 40%, due to the hydrolysis of the salt by the water. In order to investigate the effect of salt and water vapour on certain substances, these were placed in a platinum tray and inserted in the apparatus. Selected chips of quartz were rendered opaque and the sharp edges and rough surfaces were smoothed by the mixed vapour, a compound corresponding with $Na_2O:1·023SiO_2$ being formed superficially. In dry air, the quartz was much less attacked. Commercial ferric oxide was converted into magnetic iron oxide and numerous black, shining crystals in the presence of salt and water vapour at 1100°. The black crystals of magnetic iron oxide were also formed when ferric oxide was mixed with an excess of salt and heated for twelve hours in the full blast of a Teclu burner. The crystals appear to be due to the presence of salt, as they are not formed when ferric oxide is heated alone. Alumina on similar treatment became coated with a layer of fused material, which may be a sodium aluminate, $2Al_2O_3,9Na_2O$. In clays, a more deeply seated action occurs. A. B. S.

**The System Lime-Alumina-Silica and its Relation to Slags and Portland Cement.** B. NEUMANN (*Stahl u. Eisen*, 1918, **38**, 953—960).—The author summarises the results of various investigations on the binary and ternary systems of lime, alumina, and silica, and points out that the possible compositions of slags and Portland cements only occupy very small areas in the triangular diagram used to represent such ternary mixtures. He refers to J. E. Johnson, jun.'s (*Met. and Chem. Eng.*, 1916, 363), curve showing the composition–temperature relations for freely flowing slags and its general identity with mixtures of the pure oxides of the same compositions, and suggests that a further study of such mixtures may have far-reaching consequences

Mixtures corresponding with Portland cements occupy an extremely small area in the triangular diagram, and the position of this area renders untenable the various theories which are based on the existence of a ternary compound in Portland cements. The author accepts Rankin's suggestion (*J. Franklin Inst.*, 1916, 181) that Portland cement is produced by the formation of the compounds $2CaO,SiO_2$ and $5CaO,3Al_2O_3$, which absorb lime and form tricalcium silicate and tricalcium aluminate. The former is regarded as the essential constituent of the cement, the latter acting chiefly as a flux or solvent which reduces the temperature at which the former is produced. Further investigations with a view to discover other solvents, together with a study of the effect of replacing alumina by iron oxide, are suggested. [See also *J. Soc. Chem. Ind.*, December, 1918.] A. B. S.

**The Carbides of the Rare Earths of the Cerium Group.** A. DAMIENS (*Ann. Chim.*, 1918, [ix], **10**, 137—183).—A study of the action of water on the carbides of cerium, lanthanum, neodymium, praseodymium, and samarium. The gas evolved in every case consisted of a mixture of hydrogen, saturated hydrocarbons, ethylenic and acetylenic hydrocarbons. The proportion of hydrogen was in all cases high. In no case was any methane found, the saturated hydrocarbons consisting of ethane, propane, and *iso*butane. The ethylenic hydrocarbons consisted of ethylene and its homologues, and the acetylenic hydrocarbons of acetylene and its homologues. The different constituents of the mixture were invariably present, but their relative proportions varied according to the velocity of the reaction, which was dependent on the physical state of the carbide.

The metallic hydroxides produced were always those of the sesquioxides. *Cerous hydroxide* was isolated as a white substance, which fixes oxygen in the cold with the development of heat and the formation of ceric hydroxide. W. G.

**Gallium.** L. M. DENIS and J. ALLINGTON BRIDGMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 1531—1561).—See this vol., ii, 456.

**The Heterogeneity of Steel.** H. LE CHATELIER and B. BOGITCH (*Compt. rend.*, 1918, **167**, 472—477).—The macrographic etching of steel shows a heterogeneous structure which is unaltered by heat treatment, as distinguished from the micrographic etching. Macrographic heterogeneity is due to oxygen in solid solution in the metal, and phosphorus or sulphur has no direct influence. The difference in the value of the electrical resistivity of steel as calculated from the chemical composition (excluding oxygen) and

as actually determined is considered to be due to the presence of oxygen in the steel. [See, further, *J. Soc. Chem. Ind.*, 701A.]
C. A. K.

**The Metallographic Examination of Tinplate.** L. Mayer (*Stahl u. Eisen*, 1918, **38**, 960—962).—It is commonly thought that the adhesion of tin to iron in tin-plate is due to the formation of a compound of the two metals. The author has examined pieces of commercial tin-plate with negative results. He immersed small cubes of iron of high and low carbon content in tin at various temperatures, and on examining these under the microscope found a layer of intermediate crystals, the thickness of the layer varying with the temperature of immersion. At 500°, part of the pearlite in the high carbon iron and at 750° that in the low carbon iron disappeared, but reappeared around the edges of the tin at 950°. From this, the author concludes that the diffusion of tin and iron at various temperatures may be indirectly traced by the behaviour of the pearlite and ferrite forms of iron at high temperatures. [See also *J. Soc. Chem. Ind.*, 736A.]
A. B. S.

**Formation of Iron Disulphide by Wet Methods.** V. Rodt (*Mitt. K. Materialprüf.*, 1918, **36**, 93—107).—The first product of the action of hydrogen sulphide on iron hydroxide is iron trisulphide; if the reaction is carried out at a higher temperature, this is decomposed with the formation of iron disulphide, $FeS_2$, which is insoluble in hydrochloric acid. As thus obtained, iron disulphide has $D_4^{18}$ 4·588, which is nearer to that of marcasite (4·55 to 4·88) than to that of pyrites (4·9—5·2). The reaction, $Fe_2S_3 \longrightarrow FeS_2 + FeS$, does not take place in the presence of substances having an alkaline reaction. Iron disulphide may also be obtained by boiling freshly prepared iron monosulphide, suspended in water, with sulphur in the absence of alkaline substances. These reactions would account for the formation of iron disulphide in soils containing iron hydroxide compounds and putrescent matter and free from alkaline earth carbonates. [See also *J. Soc. Chem. Ind.*, 732A.]
C. A. M.

**Crystal Structure of Grey Tin.** A. J. Bijl and N. H. Kolkmeyer (*Chem. Weekblad*, 1918, **15**, 1264).—Grey tin has a crystalline structure, the crystals belonging to the cubic system. The tin atoms are arranged similarly to the carbon atoms in diamond.
A. J. W.

**Galvanic Potential of Alloys.** G. Tammann (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 345—372; from *Chem. Zentr.*, 1918, ii, 265—267).—Mixed crystals show resistance limits towards galvanic polarisation as well as towards chemical reagents (A., 1917, ii, 448). It was desirable to investigate the connexion between the potential of alloys and their composition, since the thermodynamic theory denies the possibility of the existence of galvanic resistance limits.

According to this theory, the metallic phase is in equilibrium with the electrolyte, so that even in the metallic phase the change of position of the two kinds of atoms is sufficiently frequent for the establishment of a definite concentration. This condition is not fulfilled at temperatures at which chemical resistance limits occur. The thermodynamic theory is developed for a homogeneous binary metallic mixture, and a number of the conclusions are experimentally verified. Silver–gold mixed crystals were investigated with the electrometer, using the system $Ag|0{\cdot}02AgNO_3|0{\cdot}1KNO_3|0{\cdot}01AuCl_3|Au$; the potential of the open system is definite. When the silver electrode is replaced by alloys of silver and gold, the potential is found to depend on the previous history of the alloy; the results can be interpreted by assuming that Ag–Au atoms are unable to change places with one another. The Ag atoms are superficially removed by boiling nitric acid, and the surface behaves then as if composed of gold. If the surface is rubbed with emery, a portion of the superficial gold is removed and the silver atoms again come to the surface. The behaviour of plates with untouched surfaces after prolonged tempering is unexpected; the potential of silver is first exhibited, which rapidly decreases, approximates to the potential of gold, and finally, after eighteen hours, increases to that of silver. The potential at which noticeable polarisation occurs is, within the limits of error, the same for gold and for gold–silver alloys with more than 0·5 mol. Au; this is particularly marked for $NO_3$ anions. The gold content at which the polarisation potential decreases (0·5 mol. Au) is independent of the valency of the polarising anion, whilst with chemical agents it depends on the number of Ag atoms which react with a molecule of the reagent. With a gold content less than 0·5 mol., polarisation is greatly dependent on the treatment of the electrodes. The galvanic and chemical resistance limits for 0·5 mol. Au are identical for simple reagents. If the structure of a series of metallic conglomerates is unknown, no conclusion can be drawn from the relationship between the potential line and the composition as to whether the conglomerate consists of one or two types of crystals in those regions of concentration in which the potential is independent of the concentration, neither is the sudden alteration of potential with alteration of concentration a sign of the formation of a new type of crystal. Such conclusions are only justified when the atoms are sufficiently mobile, as is the case with Au–Ag alloys at 320°, when a continuous alteration of the potential with the concentration is observed. The work of other authors also shows that the potential of a series of mixed crystals alters continuously with the concentration when diffusion is sufficiently rapid, and that the potential of a series of alloys with two types of crystal is independent of the concentration (Cd amalgams); when, however, diffusion is not sufficiently rapid to keep the surface concentration definite, the potential is either independent of the concentration or alters very rapidly, the alteration beginning at a concentration corresponding with multiple proportions. The galvanic limits are also those of the precipitation of other metals from their solution. The non-resistant and the relatively resistant mixed crystals are distinguished in their precipitating ability, since the former also precipitate those metals the potentials of which lie between the true values of the unchanged surface of the resistant and that of the relatively resistant mixed crystals. Thus, Ag–Zn mixed crystals with less than 0·25 mol. Ag precipitate all metals from zinc onwards, whilst those with more than 0·25 mol. Ag, the potential of which towards zinc is more than 0·6 volt, only precipitate lead and the following metals.

The resistance limits of Au–Ag mixed crystals are considered from the space lattice theory. The condition of the less noble metal in a series of mixed crystals can be deduced from the value of the potential at which it passes into solution. If it dissolves at its own potential, it is present in the free state and a second galvanic limit cannot occur (Cu–Au and Ag–Au mixed crystals), if it dissolves at a lower potential, it is present in the combined state, and a second resistance limit may be found (Zn–Au mixed crystals with 0·17—0·37 mol. Au, from which it follows that the crystals from 0·43—0·64 Au contain the compound AuZn). The difference between a mixed crystal and a chemical compound depends on the electrons surrounding the positive core. H. W.

**The Limits of the Gold Content within which Copper–Gold and Silver-Gold Mixed Crystals are attacked by Chemical Reagents.** G. Tammann (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 385—425; from *Chem. Zentr.*, 1918, ii, 268—270. Compare preceding abstract).—The resistance limits of the mixed crystals mentioned above have now been determined with greater accuracy than in the case of the previous investigation (A., 1917, ii, 448), and it is now possible, in the most favourable cases, to define these limits for differences of concentration as low as 0·001 mol. Au. The degree of accuracy depends chiefly on the distinctness of the alteration caused by the agent on the surface, and the separation of an opaque, slightly soluble product is advantageous. Accuracy is favoured by evenness and uniformity of surface. In the crystallisation of mixed crystals, it is general to find a difference between the compositions of the molten residue and of the crystals which causes lack of homogeneity in the conglomerate, so that the latter is not uniformly coloured by a chemical reagent. This defect can be greatly remedied by tempering, preferably at a high temperature, and also by rolling. The influence of the duration of tempering on the uniformity of the alloy was particularly investigated with an Ag–Au alloy containing 0·49—0·51 mol. Au; after ordinary cooling, in which the temperature interval 1000—300° was passed through in fifteen minutes, the alloy showed no particles in which the percentage of gold differed by more than 0·75% from the mean value; after tempering for four hours at 700°, differences of concentration equivalent to 0·005 mol. Au remained.

The action of palladium chloride solution (4%) on Cu–Au alloys with 0·23—0·27 mol. Au has been studied; the plates with natural surfaces precipitate palladium when containing less than 0·25 mol. Au, and this limit is easily perceived with a difference of less than 0·005 mol. Au. The action of palladium nitrate on Ag–Au alloys, and of platinous chloride on Cu–Au and Ag–Au alloys, is also described. Cu–Au mixed crystals with 0·282 Au and more remain untarnished for a year in yellow ammonium sulphide solution, whereas alloys with 0·243 and less Au are completely blackened after a few hours or days; in this respect, mixed solutions of ammonium sulphide and disulphide act most rapidly, followed in order by solution of sulphur in sodium sulphide, sodium sulphide solution, and solution of sulphur in carbon disulphide. The sequence of darkening, previous to tempering for twelve hours at 720°, did not correspond with the copper content; after such tempering, the tendency to darkening decreased regularly with increasing gold content. The action of sodium sulphide only occurs in presence of oxygen, whilst with polysulphide solutions this is unnecessary. The limit of deep-seated action of $Na_2S_2$ solution on Cu–Au crystals lies between 0·245 and 0·255 mol. Au; with polished plates, it is slightly more than 0·270 Au. The same solutions were used with Ag–Au mixed crystals; in this case, darkening with ammonium disulphide solution occurs far more regularly. Increase in the period of tempering diminishes the rapidity of the action. Sodium disulphide solution behaves similarly, but more rapidly. The previous datum, that mild oxidising agents, such as hydrogen peroxide, air, alkaline sodium tartrate, or picric acid, are active up to a gold content of 0·243 mol. cannot be fully maintained; the limit is now found at about 0·22 mol. For powerful oxidising agents, the following limits were observed: $AuCl_3$ (0·495—0·505 mol. Au); $H_2CrO_4$ (0·492); $HMnO_4$ (0·495—0·505); $HNO_3$ (0·480—0·490). Mercurous salts react with the complete series of Cu–Au alloys, but not with pure gold. The rate of action increases with the concentration of the solution, with which, also, the nature of the alteration of the plate varies. Alloys containing up to 0·24 mol. Au precipitate mercury from mercuric chloride solution, whilst those richer in gold precipitate mercurous chloride. Silver salts have a limit of 0·05—0·15 for Cu–Au alloys, but precipitation occurs at isolated spots, from which, with simple salts, needles or leaflets grow with visible rapidity. The limits vary with the nature of the negative ion, and vary considerably round a gold content of $\frac{1}{8}$ mol. The limits of precipitation with hard, untempered plates lie at a slightly higher gold content than for tempered plates. It is generally observed that the action of a reagent with distinct limits is noticeable after a few days, and does not then change after several months. The superficial nature of the alloy is of great importance for the action limits; the natural surface is the most resistant. If the alloy is rubbed with the finest emery paper, numerous scratches are formed at the surfaces, of which the usual distribution of the atoms in the lattice is disturbed. The distribution of the atoms, caused by grinding and polishing, approximates to the unarranged, which is far less resistant than the normal distribution. In many cases, protective layers are formed during tempering, which can be recognised by the diminution of the time of attack with increasing period of tempering. The numerical values of the action limits are partly multiples of one-eighth within the limits of experimental error; at times these multiples are not quite attained, whilst at others they are noticeably exceeded.

The various reagents are classified with respect to action limits, and attempts are made to explain the actions of mixed crystals by means of lattice models. H. W.

**Behaviour of Mixed Crystals of Copper, Silver, and Gold towards Chemical Reagents and the Colour of these Mixed Crystals.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 373—384; from *Chem. Zentr.*, 1918, ii, 267—268. Compare preceding abstracts).—The problem of the resistance limits of ternary mixed crystals is of interest from the theoretical standpoint and also from the practical point of view of the possibility of the partial replacement of the noble metal of a binary resistant alloy with the formation of an equally resistant ternary mixture. The experiments described have been performed with Cu, Ag, Au alloys, since the resistance limits of the binary systems have been investigated. A series of mixed crystals has been prepared in which the atomic ratios Ag to Cu has been kept constant at 1:2, 1:1, and 2:1, respectively, whilst the amounts of gold were increased by 0·05 mol. between 0·20 and 0·55 mol. In the case of the second of the series, the alloys were investigated in the hard and soft states, but, as no noticeable differences were observed, the remaining alloys were only used in the latter condition. In contrast to the author's experience with binary alloys (A., 1917, ii, 448), the resistance limits with ternary alloys are more or less indefinite, and it is necessary to distinguish between the limits of deep-seated and superficial action; the latter is commonly associated with a much higher gold content than the former, and this is particularly marked in the cases of the action of concentrated nitric acid and of a mixture of chromic and sulphuric acids. The action limits of the following reagents on the ternary alloys have been investigated: ammonium disulphide, palladium chloride and nitrate, picric acid, potassium dichromate and sulphuric acid, nitric acid, gold chloride, permanganic and sulphuric acids. In respect of deep-seated action, the ternary alloys are generally more noble than the binary.

A number of observations on the colour of ternary alloys are schematically recorded. The distribution of the different types of atoms in a 14-point lattice is also discussed. H. W.

## Mineralogical Chemistry.

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**Pyrolusite from Virginia.** THOMAS L. WATSON and EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1918, **8**, 550—560).—The manganese ore mined in Little Fork Valley, near Woodstock, in Shenandoah Co., occurs as an impregnation and replacement in brecciated sandstone and conglomerate in the trough of a syncline. It consists mainly of crystalline, fibrous pyrolusite with some wad. Small crystals are abundant, lining cavities. The colour is black, but steel-grey on fresh fractures, with metallic lustre; streak, black to slightly bluish-black. H. 2½. Anal. I is of crystals and II of crystalline, fibrous material.

| | $MnO_2$. | MnO. | $Fe_2O_3$. | $Al_2O_3$. | BaO. | CaO. | $SiO_2$. |
|---|---|---|---|---|---|---|---|
| I. | 94·30 | 2·25 | 0·22 | 0·14 | 0·33 | 0·08 | 0·64 |
| II. | 95·22 | 1·31 | 0·17 | 0·18 | 0·40 | 0·11 | 0·63 |

| | $P_2O_5$. | $H_2O$ ($>$105°). | $H_2O$ ($<$105°). | Total. | Sp. gr. |
|---|---|---|---|---|---|
| I. | 0·52 | 1·53 | 0·22 | 100·23 | 4·748 |
| II. | 0·58 | 1·46 | 0·16 | 103·22 | 4·885 |

The material thus has the physical characters and composition ($MnO_2$) of pyrolusite, but, as usual, the crystals have the orthorhombic form and habit of manganite. The axial ratios, $a:b:c=0·8616:1:0·5628$, however, differ somewhat from those usually accepted for manganite (0·8441 : 1 : 0·5448), although they are very close to the value for manganite from Böhlet, Sweden (0·8612 : 1 : 0·5629, G. Flink, 1900). It is thus just possible that these are original crystals of pyrolusite rather than pseudomorphs after manganite, as commonly believed. L. J. S.

**Deposits of Potassium Salts at Dallol (Eritrea).** M. GIUA (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 331—335; *Gazzetta*, 1918, **48**, ii, 1—8).—The results are given of analyses of a number of samples from the salt deposits of Dallol, in S. Dancalia (Eritrea). At many points these deposits consist largely of potassium chloride (up to 98·6%), whilst at others sodium chloride predominates. In both cases, the proportions of magnesium chloride are low, and only traces of bromides are present in a few instances. The potassium minerals occur at the surface of the earth and are localised at certain points of the salt area. The thermal springs of Dallol have a temperature of about 80—90°, and consist of saturated solutions of magnesium chloride containing traces of sodium chloride and appreciable proportions of magnesium bromide. T. H. P.

**Etching of Gypsum by Concentrated Sulphuric Acid.** ROMAN GRENGG (*Tsch. Min. Mitt.*, 1915, **33**, 201—226; from *Jahrb. Min.*, 1918, Ref. 135—136. Compare A., 1915, ii, 450).—Crystals of gypsum immersed in concentrated sulphuric acid develop on the faces flat hillocks with a more or less elliptical outline. This type of etch-figure is described as 'etch-shield,' as distinct from 'etch-hill.' The solution of the gypsum gives rise momentarily to a supersaturated solution of $CaH_6(SO_4)_4$, from which are deposited microscopic aggregates, probably of the hemihydrate, $CaSO_4,\frac{1}{2}H_2O$. The process proceeds with the formation of mainly the monoclinic salt, $CaH_6(SO_4)_4$, together with the acid salt, $CaH_2(SO_4)_2$. After a time, the process becomes slower, and spaces corresponding with the 'etch-shields' appear in the covering layer of acid calcium sulphate. At a later stage, the acid acts by extracting water from the gypsum, with the production of the characteristic weathering surfaces, until, finally, the whole crystal is transformed into anhydrous calcium sulphate. The 'etch-shields' approximate to the position of the plane (807), perpendicular to which is the greatest solubility in the concentrated acid.

L. J. S.

**The Constitutional Formula of Nephelite.** ST. J. THUGUTT (*Spraw. Tow. Nank. Warszaw., Math.-naturw. Kl.*, 1913, **6**, 849—862; from *Jahrb. Min.*, 1918, Ref. 132—133).—The author defends the formula $8Na_2Al_2Si_3O_{10},4Na_2Al_2O_4,3K_2Al_2Si_3O_{10}$ previously proposed by him (A., 1895, ii, 358), and criticises later views (A., 1911, ii, 122, 992; 1912, ii, 176, 569). Morozewic's formula, $K_4Na_{18}Al_{22}Si_{23}O_{90}$ (A., 1908, ii, 202), for 'basic' nephelite can be expressed as

$$18Na_2Al_2Si_3O_{10},9Na_2Al_2O_4,K_2Al_2O_4,5K_2Al_2Si_3O_{10}.$$

By the action of superheated water, nephelite splits up into natrolite ($Na_2Al_2Si_3O_{10},2H_2O$), gibbsite [$Al(OH)_3$], and muscovite [$H_2KAl_3(SiO_4)_3$], whilst some of the sodium goes into solution, these minerals corresponding in composition with the three molecules in the author's formula. It is suggested that the variations in analyses of nephelite may be due to want of homogeneity of the material, and that the secondary minerals mentioned above may be present in an extremely finely divided state. L. J. S.

## Analytical Chemistry.

**The Use of Thymolsulphophthalein as an Indicator in Acidimetric Titrations.** ARTHUR B. CLARK and HERBERT A. LUBS (*J. Amer. Chem. Soc.*, 1918, **40**, 1443—1448. Compare A., 1916, ii, 44, 570).—Thymolsulphophthalein, an indicator having two useful working ranges, can be very successfully employed in many differential acidimetric and alkalimetric titrations. To illustrate the general method of employment, a few typical titrations are given (mixtures of benzoic and hydrochloric acids, acetic and hydrochloric acids, acetic and sulphuric acids, titration of aniline by hydrochloric or sulphuric acid). Any acid with a dissociation equal to or weaker than that of acetic acid may be differentially titrated in the presence of hydrochloric acid, provided that the weaker acid is completely neutralised when the alkaline colour change of the indicator occurs.

The use of proper colour screens or, preferably, of a colorimeter or spectrophotometer, greatly increases the accuracy of differential titrations, but is not absolutely necessary. H. W.

**Titration of Free Hydrochloric Acid in Gastric Juice with Suppression of the Dissociation of Organic Acids by Addition of Alcohol.** GEORG KELLING (*Berl. klin. Woch.*, 1918, **54**, 334—336; from *Chem. Zentr.*, 1918, i, 1063—1064).—The use of dimethylaminoazobenzene, Congo-red, or tropæolin for the detection of free hydrochloric acid is rendered uncertain by the presence of large amounts of organic acids or of loosely combined hydrochloric acid. The author recommends the following process, which, in a simple manner, gives results which are in close agreement with those obtained by Günzburg's method. Two drops of a 0·5% solution of dimethylaminoazobenzene in alcohol (90%) are added to 5 c.c. of gastric juice; an intense carmine-red coloration denotes the presence of free hydrochloric acid. 7·5 C.c. of alcohol (96%) are added, and the solution is titrated with *N*/10-potassium hydroxide until a pure yellow shade is obtained. (If more than 2·5 c.c. of alkali are required, it should be observed that the volume of added alcohol must be approximately half that of the aqueous liquid.) The acidity of 10 c.c. is calculated by multiplying by 2 and adding 3. The addition is necessary, since the alcohol affects the acidity of free hydrochloric acid for the indicator to this extent. When free hydrochloric acid is absent and the hydrochloric acid deficit is to be estimated, a similar process is adopted—an equal volume of alcohol is added, followed by hydrochloric acid, until a red coloration is produced; the solution is then titrated back with *N*/10-potassium hydroxide. The two acid values are subtracted, the difference is calculated to 10 c.c., and increased by three. The added alcohol completely suppresses the acidity of organic acids so far as the reaction is concerned.

H. W.

**Colorimetric Scale for the Estimation of Free Hydrochloric Acid [in Gastric Juice] by means of Brilliant-Green.** M. DELORT and ROCHE (*Compt. rend. Soc. Biol.*, 1918, **81**, 646—649).—An unfiltered 1% solution of methylene-blue in dilute alcohol, a 5% aqueous solution of normal potassium chromate, and an unfiltered 0·1% solution of eosin in dilute alcohol are mixed with water in six given proportions. The mixtures are kept in sealed tubes, and constitute a permanent scale of colours which match those produced by mixing equal volumes of a 0·02% solution of brilliant-green with gastric juice containing six different concentrations of free hydrochloric acid (0·025% to 0·2%). G. B.

**I. Detection and Separation of Hydrochloric Acid in Presence of Bromic and Iodic Acids. II. Detection and Estimation of Bromic and Iodic Acids in Presence of Hydrochloric, Hydrobromic, and Hydriodic Acids.** ATTILIO PURGOTTI (*Gazzetta*, 1918, **48**, ii, 63—66).—The methods here proposed are based on the fact that potassium or sodium hydroxide attacks silver bromate and iodate in the cold, whereas silver chloride, bromide, and iodide remain unchanged. [See *J. Soc. Chem. Ind.*, 730A.] T. H. P.

**Estimation of Hypochlorite and Chlorate in the same Mixture.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 1289—1295).—The estimation of hypochlorite and chlorate in such a substance as bleaching powder is carried out as follows.

To 25 c.c. of *N*/10-arsenious oxide solution are added 5 c.c. of 4*N*-acetic acid and three drops of 0·2% methyl-red. The hypochlorite solution is then run in until the liquid is decolorised, the number of c.c. used containing 88·75 mg. of active chlorine.

To the colourless solution thus obtained are added 25 c.c. of the arsenious oxide solution and 20 c.c. of concentrated hydrochloric acid, and the mixture boiled for five minutes. The excess of arsenious oxide is then estimated by titration with *N*/10-potassium bromate, each c.c. of arsenious oxide solution used corresponding with 1·4 mg. of $ClO_3$ or 3·45 mg. of active chlorine. A. J. W.

**Estimation of Sulphuric Acid and Barium as Barium Sulphate.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 212).—A reply to Karaoglanow (this vol., ii, 369). W. P. S.

**Volumetric Estimation of Sulphates.** VANSTEENBERGER and BAUZIL (*Ann. Chim. anal.*, 1918, **23**, 210—214).—The solution containing a sulphate is heated at 60—70° with an excess of sodium carbonate solution, filtered, the filtrate slightly acidified with hydrochloric acid, and treated with an excess of standardised barium chloride solution. The mixture is boiled for one minute, filtered, and the excess of barium in the filtrate precipitated as barium carbonate, which is collected, washed, and titrated with *N*/10-hydrochloric acid, using methyl-orange as indicator. [See, further, *J. Soc. Chem. Ind.*, 689A.] W. P. S.

**Volumetric Estimation of Selenious Acid and Selenic Acid.** L. MOSER and W. PRINZ (*Zeitsch. anal. Chem.*, 1918, **57**, 277—305).—The iodometric estimation of selenious acid is trustworthy if the selenious acid is heated in a distillation flask with four times the theoretical quantity of potassium iodide in the presence of hydrochloric acid, and the liberated iodine titrated in the receiver and in the residue. The indirect iodometric method described by Gooch and Pierce (A., 1896, ii, 334) is also trustworthy if carried out as a distillation process. Oxidation with permanganate in alkaline solution as proposed by Marino (A.,

1910, ii, 155) is untrustworthy if the oxidation mixture is acidified before cooling. Titration of selenious acid with titanium trichloride solution does not give accurate results, owing to the formation of a quantity of hydrogen selenide. Reduction with hydriodic acid is the most trustworthy method for the estimation of selenic acid. [See, further, *J. Soc. Chem. Ind.*, 730A.]
W. P. S.

**Estimation of Nitrogen in Urine by Kjeldahl's Method.** C. Oehme and M. Oehme (*Ber. Klin. Woch.*, 1918, **55**, 401—402; from *Chem. Zentr.*, 1918, ii, 70).—To economise reagents, gas, and time, the authors recommend a reduction in the quantities usual for a Kjeldahl estimation, and propose the following process. Urine (1 c.c.) and concentrated sulphuric acid (2 c.c.) are heated in the usual manner after addition of potassium and copper sulphates. Distillation, after addition of water (100 c.c.) and sodium hydroxide solution (33%, 15—20 c.c.), is usually complete in fifteen to twenty minutes. *N*/20-Acid is conveniently used for titration.
H. W.

**Estimation of the Residual Nitrogen in Blood-serum.** Fischer (*Zeitsch. physiol. Chem.*, 1918, **102**, 266—274).—In the estimation of the residual nitrogen in blood-serum, it is essential that the proteins should be so completely removed by precipitation that no trace of the latter can be detected in the filtrate. This result can be achieved by precipitating with sodium acetate or chloride in the presence of acetic acid at 100°, or by treatment with uranium acetate at the ordinary temperature. The author recommends the uranium acetate method, which yields values for the residual nitrogen varying from 20 to 90 mg. of nitrogen per 100 c.c. of blood-serum.
H. W. B.

**Estimation of Minimal Quantities of Nitrites and Hydrogen Peroxide, either Separate or Present together.** A. Quartaroli (*Gazzetta*, 1918, **48**, i, 102—111).—Less than one part of nitrite per million of water may be detected by the blood-red coloration given by a reagent containing potassium thiocyanate, ferrous sulphate, and nitric acid. The same reaction is given by hydrogen peroxide, potassium persulphate, and probably other peroxygenated compounds, but not by chlorates or perchlorates. With hydrogen peroxide, the coloration produced is less intense than that with nitrous acid, but the reaction is more sensitive than any other for the peroxide. With nitrous acid, but not with hydrogen peroxide, the coloration formed disappears when the solution is heated rapidly to boiling with concentrated hydrochloric acid and carbamide. [See *J. Soc. Chem. Ind.*, 731A.] T. H. P.

**Methods for the Estimation of Phosphoric Acid in Small Amounts of Blood.** W. R. Bloor (*J. Biol. Chem.*, 1918, **36**, 33—48).—The estimation of the phosphoric acid is based on its precipitation as strychnine phosphomolybdate by a modification of Kober and Egerer's method (A., 1915, ii, 794). The amount of precipitate is estimated nephelometrically. H. W. B.

**Detection, Estimation, and Elimination of Arsenic and Mercury in Urine.** PAUL DURET (*Compt. rend. Soc. Biol.*, 1918, **81**, 736—737, 737—739).—See this vol., i, 561.

**Microchemical Notices.** O. TUNMANN (*Pharm. Post.*, 1918, **51**, 341—342, 353—354; from *Chem. Zentr.*, 1918, ii, 401—402. Compare this vol., ii, 465).—II. *Occurrence of a Crystalline Substance in the Seeds of* Strychnos nux vomica, L.—In a single instance out of several hundred seeds examined, considerable quantities of colourless needles of chlorogenic acid were observed.

III. *Identification of Arsenious Acid.*—The extension of microchemical methods to chemical preparations is considered a hasty step by the author (contrast Wasicky and Mayrhofer, *Zeitsch. allg. Österr. Apoth. Ver.*, **55**, 305); the method should be restricted to drugs. Arsenious acid is best detected by sublimation from an asbestos plate at a comparatively high temperature; the method can be applied directly to powders, pills, and even to ointments. Destruction of organic matter, if necessary, can be conveniently effected by heating the material with sulphuric acid on the object-glass. The sublimed arsenious oxide crystallises in octahedra, tetrahedra, and, not infrequently, in monoclinic prisms. Should the crystals be small, addition of a little water or glycerol causes the formation of larger crystals. The sublimate should always be tested with silver nitrate; for this purpose, it is dissolved in warm water beneath the cover-glass; on one side of the latter a drop of 0·1% silver nitrate is added, and on the other side a drop of very dilute ammonia. A chrome-yellow precipitate, which slowly becomes brownish-yellow, is formed at the junction of the liquids. H. W.

**Silver-asbestos, Lead Chromate-asbestos and Lead Peroxide-asbestos.** O. BINDER (*Chem. Zeit.*, 1918, **42**, 522).—A mixture of asbestos and finely divided metallic silver may be used for the absorption of chlorine in the combustion of organic substances; asbestos mixed with lead chromate or peroxide serves for the absorption of sulphur compounds. The silver is prepared by reducing ammoniacal silver nitrate solution with zinc. [See, further, *J. Soc. Chem. Ind.*, December.] W. P. S.

**Errors in Alkalimetry due to the Presence of Carbon Dioxide in Distilled Water.** G. BRUHNS (*Zeitsch. anal. Chem.*, 1918, **57**, 257—277).—Attention is directed to the influence of dissolved carbon dioxide in water and in standard acid and alkali solutions on acidimetric and alkalimetric titrations. [See, further, *J. Soc. Chem. Ind.*, 730A.] W. P. S.

**The Iodotannic Reagent.** D. E. TSAKALOTOS and D. DALMAS (*Bull. Soc. chim.*, 1918, [iv], **23**, 391—400).—The reagent is a mixture of 1 c.c. of $N/10$-iodine solution with 1 c.c. of a 1% tannin solution, and is used to determine the alkalinity of very dilute alkaline solutions. The procedure is as follows. To the 2 c.c. of reagent in a porcelain dish, the alkaline solution is added with stirring until a definite red colour appears. From this point, the alkaline solution is run in gradually, and, after each addition, a drop of the mixture is tested on starch-paper. The end-point is reached when a blue colour is no longer formed on the test-paper. From a table given in the original, the alkalinity of the solution may then be calculated, knowing the volume of solution used. By means of this reagent exact results may be obtained with alkaline solutions at a dilution of $N/10,000$ to $N/40,000$.

W. G.

**Simplification in the Estimation of Potassium.** W. HÜTTNER (*Kali*, 1918, **12**, 178—179; from *Chem. Zentr.*, 1918, ii, 402—403).—The process depends on the substitution of barium bromide, $BaBr_2,2H_2O$, which is soluble in alcohol for the insoluble chloride. It is essential that the specimen of bromide should leave no residue when treated with alcohol; it is conveniently prepared from potassium bromide and barium carbonate, evaporation, and extraction of the residue with alcohol.

A weighed quantity of the potassium salt is dissolved in cold water, an excess of a highly concentrated aqueous solution of barium bromide is added, and the mixture is shaken and made up to the mark. The precipitate settles well; it is filtered, and 10 c.c. of the filtrate are treated with perchloric acid. Solution in cold water should be more generally adopted; specimens of carnallite, except as regards any kieserite, are immediately dissolved. The residue does not generally contain potassium. If this should be the case, the carnallite contains notable quantities of soluble potassium sulphates (polyhalite, langbeinite, etc.), and must be dissolved in the hot solvent. In this case, it is advisable to add hydrobromic instead of hydrochloric acid to prevent subsequent formation of barium chloride from the bromide. H. W.

**Recovery of Silver from Albumose-silver Solutions and Methods for the Analysis of the latter.** G. MAUE (*Chem. Zeit.*, 1918, **42**, 513—515).—Precipitation as chloride or thiocyanate in sulphuric acid solution is recommended for the recovery of silver from waste therapeutical albumose-silver solutions; the silver chloride or thiocyanate is subsequently collected, and fused with alkali carbonate and nitrate in order to obtain metallic silver. The most trustworthy methods for estimating the silver content of albumose-silver solutions are those based on the reduction of the silver by lactose or tannin in alkaline solution, or on its precipitation as bromide, iodide, chloride, thiocyanate, or ferrocyanide in acid solution. The precipitated silver or silver compound is then fused with alkali carbonate and nitrate, the metallic silver dissolved in nitric acid, and titrated with thiocyanate solution. [See, further, *J. Soc. Chem. Ind.*, December.] W. P. S.

**Estimation of Magnesium.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 211—212).—In the absence of large quantities of potassium chloride or sodium chloride, magnesium may be precipitated and weighed as $MgNH_4PO_4,6H_2O$. The precipitation is made at 90°, and the precipitate is collected after twenty-four hours, washed with ammonia and methyl alcohol, dried over calcium chloride, and weighed. [See, further, *J. Soc. Chem. Ind.*, 751A.] W. P. S.

**Analysis of Magnesite.** V. MACRI (*Boll. chim. farm.*, 1918, **47**, 301—302).—The volumetric method given by Merck Guano & Phosphat Werken (A., 1909, ii, 619) for analysing magnesite does not give trustworthy results. The author describes a modification of the usual method, by means of which risk of loss by projection during evaporation on a sand-bath is avoided. [See *J. Soc. Chem. Ind.*, December.] T. H. P.

**Alkali Iodides as Reagents for Cadmium and Nickel.** A. AGRESTINI (*Gazzetta*, 1918, **48**, ii, 30—34).—With a distinctly ammoniacal solution of a cadmium salt, 20—30% potassium iodide solution yields a heavy, white precipitate composed of regular octahedra and having the formula $Cd(NH_3)_2I_2$, whereas with a solution of a copper salt no precipitate forms under similar conditions. With the same reagent, strongly ammoniacal solutions of nickel salts give a heavy, bluish-violet precipitate of the formula $Ni(NH_3)_6I_2$, and consisting of microscopic, regular octahedra. Cobalt also gives a precipitate with this reagent, and must be removed before testing for nickel. [See *J. Soc. Chem. Ind.*, 751A.] T. H. P.

**Volumetric Estimation of Lead in Tin Plate.** J. DEININGER (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 66—67).—The metal is dissolved in concentrated sulphuric acid, ammonium oxalate solution is added to complete the solution of the iron, and the lead sulphate is collected and dissolved in hot 50% sodium acetate solution. Bromine is added to precipitate the lead as peroxide, and this is then collected, dissolved in sodium acetate solution, and estimated iodometrically. [See, further, *J. Soc. Chem. Ind.*, 736A.] W. P. S.

**Gravimetric Estimation of Copper by means of Sodium Nitroprusside and the Separation of Copper and Mercury.** EMIL VOTOČEK and JAN PAZOUREK (*Chem. Zeit.*, 1918, **42**, 475—476).—The solution containing the copper salt is treated with an excess of sodium nitroprusside solution acidified previously with *N*/10-sulphuric acid, the mixture is diluted to 170 c.c., shaken for two to four hours, the precipitated cupric nitroprusside then collected on a tared filter, washed with water, dried at 110°, and weighed. The precipitate contains 22·75% of copper. This method may be applied to the precipitation of copper in the presence of mercury salts provided that sodium chloride is also added to prevent precipitation of mercuric nitroprusside (compare this vol., ii, 238, 272). The mercury in the filtrate from the cupric nitroprusside may be estimated as sulphide or volumetrically, as described previously (*loc. cit.*). [See, further, *J. Soc. Chem. Ind.*, 751A.]

W. P. S.

**Iodometric Estimation of Copper.** I. M. Kolthoff (*Pharm. Weekblad*, 1918, **55**, 1338—1346).—A summary of the literature of the iodine method of estimating copper, and an account of the results obtained by varying the experimental conditions.

A. J. W.

**Gallium.** L. M. Dennis and J. Allington Bridgman (*J. Amer. Chem. Soc.*, 1918, **40**, 1531—1561).—The spark spectra and arc spectra of gallium, indium, and zinc have been studied with the object of ascertaining the amounts of each of these elements which could be detected in the presence of large quantities of the other elements by this means. It is shown that 0·0046 mg. of gallium can be detected by means of the spark spectrum, the lines $\lambda=4172$ and $4033\ \mu\mu$ being used for the purpose. In the case of indium, 0·0013 mg. may be detected by means of the spark lines $\lambda=4511$ and $4102\ \mu\mu$. In the presence of gallium, quantities of indium as small as 0·06% of the weight of the gallium are detectable by the spark spectrum, whilst in the presence of indium, quantities of gallium amounting to 0·18% of the weight of the indium may be similarly detected.

It is shown that the fractional electrolysis of a dilute solution of indium and gallium sulphates is capable of yielding perfectly pure gallium after about fourteen electrolyses. Pure gallium chloride can be obtained from mixtures of gallium, indium, and zinc by the fractional distillation of the chloride in a current of chlorine.

The methods of estimation of gallium were studied, and it is shown that precipitation as hydroxide by means of ammonia leads to low results, because of the tendency of the precipitate to adhere to the beakers. Satisfactory results are obtained by precipitating gallium hydroxide from slightly acid solutions by means of sodium azide in boiling solution. Equally good results are obtained by precipitation of the hydroxide by adding sodium sulphite to the solution and boiling vigorously for four minutes. The last method has the advantage that physiologically active gases are not given off during the boiling, and so it is more agreeable to work with.

Zinc can be estimated in the presence of gallium by adding an excess of potassium mercuric thiocyanate to a slightly acid ($H_2SO_4$) solution of the sulphates. After keeping for several hours, the precipitate of zinc mercuric thiocyanate is filtered in a Gooch crucible and dried at 105—110°. The filtrate is acidified with hydrochloric acid and the mercury removed by hydrogen sulphide, and, after boiling to expel the excess of hydrogen sulphide, the gallium is estimated as hydroxide by means of potassium sulphite.

Mixtures of gallium and indium are separated and estimated as follows. Solutions containing small amounts of both elements are largely diluted and treated with a small amount of hydrochloric acid, and then exactly neutralised with sodium hydroxide, an excess of 1·5 grams of sodium hydroxide is added, and the solution boiled for several minutes. The precipitated indium hydroxide is well washed, dissolved in hydrochloric acid, and the process repeated. Finally, it is dissolved again in hydrochloric acid, and precipitated by ammonia, washed, dried, ignited, and weighed as oxide. The filtrates and washings from each precipitation are combined, and the gallium precipitated as hydroxide by means of sodium sulphite, as described above.

The separation of gallium and aluminium is effected in the following way. The aluminium is precipitated as hydrated chloride by adding 60 c.c. of hydrochloric acid to the solution, and then 60 c.c. of ether. The flask is immersed in cold water and the solution saturated with hydrogen chloride, when hydrated aluminium chloride is precipitated. This is filtered on a Gooch crucible, washed with a mixture of 30 c.c. hydrochloric acid and 30 c.c. ether, and then dissolved in water, and the aluminium estimated as oxide in the usual way. The combined filtrates and washings are treated with a small amount of sulphuric acid and heated to expel the ether, and most of the hydrochloric acid and the gallium estimated as oxide after precipitation with sodium sulphite. Three methods of separating and estimating mixtures of gallium, indium, and zinc, and one method of estimating mixtures of gallium, indium, zinc, and aluminium, are described. For details of these, the original paper should be consulted.

Gallium selenate has been prepared by digesting gallium hydroxide in selenic acid solution at the boiling point for several hours. After filtration, minute, very soluble crystals were obtained which show oblique extinction. The air-dried salt has the formula $Ga_2(SeO_4)_3,16H_2O$, but there is evidence that the salt which separates from water solution at the ordinary temperature is $Ga_2(SeO_4)_4,22H_2O$. The air-dried salt dissolves in water to the extent of 1 part in 1·74 parts of water at 25°. Gallium cæsium selenate alum has been prepared by crystallising a mixture of the two salts. This substance dissolves in water to the extent of 1 part in 24·1 parts of water. The solubilities of ammonium gallium, and cæsium gallium sulphate alums have been determined in water, 50% alcohol, and 70% alcohol. The following solubilities were found: ammonium gallium alum, 1 part dissolves in 3·24 parts of water, 4600 parts of 50% alcohol, and 11,400 parts of 70% alcohol; cæsium gallium alum, 1 part dissolves in 66·2 parts of water, 25,800 parts of 50% alcohol, and 28,000 parts of 70% alcohol. The solubility determinations were made at 25°.

J. F. S.

**Magneto-chemistry. Applications to Analytical Chemistry. II.** A. Quartaroli (*Gazzetta*, 1918, **48**, i, 65—78).—The method previously devised (A., 1916, ii, 123) for the estimation of magnetic salts in solution by measuring the magnetic susceptibility may be replaced by the procedure described below, which may be used with magnetic fields of moderate intensity and requires no special apparatus. By means of truncated conical poles with circular faces, a field is obtained in which a zone of great intensity is separated sharply from one of feeble intensity. The solution to be examined is introduced into a small tube of about 8 mm. internal diameter, and above it is placed, carefully and without mixing, coloured water. The tube is then arranged so that the surface of separation of the two liquids corresponds with the lower point where the poles begin to diverge. When the magnet is excited, the water bulges out into the magnetic solution beneath without sensibly mixing with it, and if the field is sufficiently intense and the susceptibility of the solution great enough, a globule of the water becomes detached and remains suspended in the magnetic liquid. The phenomenon is visible with weak fields and dilute solutions which yield scarcely perceptible indications by Plücker's or the U-tube method. Naturally, the results become more marked as the specific gravities of the two liquids approach equality.

In the application of this phenomenon to quantitative analysis, a standard solution of ferric chloride containing a little hydrochloric acid is placed in the lower part of the tube, and the solution of the ferric salt to be analysed carefully pipetted on to the top of this solution; the upper liquid is then gradually diluted with successive diminishing quantities of water until only a just perceptible bulge slowly appears; the magnet should be excited for at least a minute, and the disappearance of the phenomenon when the current is interrupted employed as a control. The results thus obtained with ferric chloride solutions of the respective concentrations 0·519, 0·2076, 0·0798, 0·0322, 0·0129, and 0·00515% were 0·5176, 0·2070, 0·0794, 0·0318, 0·0126, and 0·00500% with a field of 12,000 gauss, and 0·5181, 0·2073, 0·0795, 0·0320, 0·0127, and 0·00504% with a field of 30,000 gauss; in the latter case, a 0·002% solution gave the value 0·00184%.

As the magnetic susceptibility of ferric sulphate is, for certain concentrations, rather higher than that of the chloride, the sulphate ion should be removed by precipitation with barium chloride, followed by either filtration or decantation. The actual determination then occupies usually about fifteen minutes, and at most 2 c.c. of the liquid are necessary. The surface of separation is often visible owing to variation in the refraction, but it is convenient to add one of the ordinary indicators to the water used for dilution.

The determination of iron in this way is not affected by the presence in the solution of aluminium, phosphoric acid, etc., but if manganese or chromium salts are present, modification is necessary.

When, as is usually the case, the manganese is in small proportion, it may be determined colorimetrically and the percentage found subtracted directly from the percentage of iron found by the magnetic method, the atomic weights of the two elements and the susceptibilities of their salts differing only slightly. With marked quantities of manganese, the latter should be converted into permanganic acid, which is virtually non-magnetic; the manganese is thus determinable from the difference of the susceptibilities before and after this transformation; also, when chromium is present, this is converted into chromate, which is negligibly magnetic.

The optimum concentrations for the chromium, manganese, nickel, and cobalt solutions to be used are given, and the application of the method described to (1) volumetric analysis with permanganate, (2) volumetric analysis with dichromate, and the analysis of mixtures of chromic salts and chromates, (3) the analysis of solutions containing ferrocyanides, ferricyanides, thiocyanates, and organic matter. T. H. P.

**Influence of Iron and Organic Matter on the Iodometric Estimation of Chromium.** R. Lauffmann (*Ledertechn. Rundsch.*, 1918, **10**, 37—39; from *Chem. Zentr.*, 1918, ii, 310—311).—If oxidation is effected with sodium peroxide, the results are high in the presence of notable quantities of iron, in consequence of increased separation of iodine; when considerable amounts of hydroxides or silica are formed during fusion or subsequent acidification and are removed by filtration, the results are low, owing to adsorption of chromium. If the precipitate consists of bases which do not cause the separation of iodine and are soluble in hydrochloric acid, it is dissolved in this reagent, and the chromium is estimated in the solution. Large amounts of organic matter cause inexact results when the oxidation is effected with sodium peroxide, since, unless completely destroyed, they give rise to substances which delay the separation of iodine and cause the end-point of the titration to be indefinite. In the presence of considerable quantities of iron or organic matter, oxidation is conveniently effected with a mixture of sodium carbonate (120 parts), potassium carbonate (40 parts), and potassium chlorate (8 parts), or, in absence of organic matter, by treatment with Mohr's salt (compare Schorlemmer, this vol., ii, 372). In presence of organic matter, oxidation may be achieved with potassium permanganate (compare Schorlemmer, *loc. cit.*), and the chromium may be estimated in the filtrate. H. W.

**Analysis of Molybdenum Compounds by Volatilisation in a Current of Carbon Tetrachloride Vapour.** Paul Jannasch and Otto Laubi (*J. pr. Chem.*, 1918, [ii], **97**, 154—181).—The molybdenum compound is heated at 400° to 560° in a current of carbon tetrachloride vapour; the molybdic acid volatilises, and is collected in a receiver, evaporated with nitric acid, ignited, and weighed. The method is generally applicable to molybdates and ores, and may be used for the analysis of ferromolybdenum and molybdenum silicide; in the case of the last two compounds, silicon and iron also volatilise, and are separated subsequently from the molybdic acid. [See, further, *J. Soc. Chem. Ind.*, 732A.]

W. P. S.

**Analysis of Tungsten Compounds by Volatilisation in a Current of Carbon Tetrachloride Vapour.** PAUL JANNASCH and ROBERT LEISTE (*J. pr. Chem.*, 1918, [ii], **97**, 141—153).—Tungstic acid is readily volatilised when heated in a current of carbon dioxide saturated with carbon tetrachloride vapour. The volatilised substance is collected in a receiver, and subsequently evaporated with nitric acid, ignited, and weighed. The method may be applied to the estimation of tungsten in ammonium tungstate, sodium tungstate, calcium tungstate, lead tungstate, scheelite, wolframite, etc. [See, further, *J. Soc. Chem. Ind.*, 732A.]

W. P. S.

**A Method for the Rapid Analysis of Mixtures of Chlorinated Toluene.** HERBERT A. LUBS and ARTHUR B. CLARK (*J. Amer. Chem. Soc.*, 1918, **40**, 1449—1453).—The sample (about 0·5 gram) is placed in a sealed tube with water (10 c.c.) and briskly shaken in a bath of boiling water for two hours; the contents of the tube are washed into a small assay flask, and the tube is rinsed out with water (free from carbon dioxide) and with alcohol if any benzoic acid remains. The solution is then titrated with alkali in the presence of thymolsulphophthalein according to the authors' method (this vol., ii, 449). The percentage of benzotrichloride ($x$) is calculated from the benzoic acid formed; the percentages of benzylidene chloride ($y$) and benzyl chloride ($z$) are derived from the following relations: $x+y+z=100$; $0{\cdot}545x+0{\cdot}434y+0{\cdot}281z=$ per cent. side-chain chlorine. The method is very suitable for plant control work, and, if certain precautions are taken (*loc. cit.*), will give a high degree of accuracy.

H. W.

**New Method of Determining the Amount of Methyl Alcohol in Mixtures of Ethyl and Methyl Alcohols.** WILLIAM G. TOPLIS (*Amer. J. Pharm.*, 1918, **90**, 636—640).—The method is designed principally for the rapid testing of denatured spirits, and is based on the measurement of the volume of hydrogen evolved by sodium from the alcohol previously dehydrated by treatment with fused potassium carbonate. The determination is carried out by comparison with a sample of denatured alcohol of known composition, so that a correction for temperature and pressure of the gas is not necessary. The sodium on the end of a needle is suspended by a thread passing through the gas-leading tube. The reaction is carried out in a test-tube, to which six drops of the alcohol to be tested are added. The gas is evolved when the thread is released, after bringing the gas-delivery orifice under an inverted burette filled with light petroleum and supported in a hydrometer jar containing the same liquid. [See, further, *J. Soc. Chem. Ind.*, 711A.] J. F. B.

**Colorimetric Estimation of Phenols in the Blood.** STANLEY R. BENEDICT and RUTH C. THEIS (*J. Biol. Chem.*, 1918, **36**, 95—98).—The method consists in removing the proteins by boiling with dilute acid and alumina cream, and then estimating the total phenol + uric acid by a modification of the method of Folin and Denis (A., 1912, ii, 1011), using the phosphotungstic–phosphomolybdic reagent, excess of sodium carbonate, and, in addition, sodium hydrogen sulphite, which has a marked clarifying action. The colour is compared with that obtained from a standard resorcinol solution (0·581 mg. in 5 c.c., equivalent to 0·5 mg. of phenol in 5 c.c.), which may be preserved unchanged for several months. The uric acid is then estimated in another sample of the blood, and the difference gives the required content of phenol in the blood. H. W. B.

**Colorimetric Estimation of Cholesterol in Blood; Estimation of Coprosterol in Fæces.** VICTOR C. MYERS and EMMA L. WARDELL (*J. Biol. Chem.*, 1918, **36**, 147—156).—One c.c. of the blood, plasma, or serum is mixed with plaster of Paris and, after drying, directly extracted with chloroform. The extract containing the cholesterol is treated with acetic anhydride and concentrated sulphuric acid, and the colour which develops is compared with a standardised aqueous solution of naphthol-green B.

For the estimation of coprosterol, the fæces are treated with calcium and sodium hydroxides to saponify fats and remove bile pigments, and the residue is mixed with plaster of Paris and extracted with chloroform, as indicated for the estimation of cholesterol in the blood. Normal human blood contains from 0·100 to 0·164% of cholesterol. H. W. B.

**Estimation of Aldose Sugars by means of Iodine in Alkaline Solution. Applications.** H. COLIN and O. LIÉVIN (*Bull. Soc. chim.*, 1918, [iv], **23**, 403—405).—A slight modification of Bougault's method (compare A., 1917, ii, 395), the alkaline solution used containing 35 grams of sodium phosphate and 50 c.c. of *N*-sodium hydroxide per litre. An *N*/10-solution of iodine is used, and considerable excess added, the volume of alkaline solution used being double that of the iodine solution. The reaction is complete after one hour, and the excess of iodine is titrated back after making the solution just acid with sulphuric acid. Satisfactory results were obtained with the roots or tubercles of artichokes and chicory. W. G.

**[Estimation] of Formic Acid, Acetic Acid, and Lactic Acid [in Admixtures].** ISENOSUKE ONODERA (*Ber. Ōhara Inst. landw. Forsch.*, 1917, **1**, 231—269).—The three acids are extracted with ether from their aqueous solution; a portion of the extract is oxidised with permanganate in alkaline (sodium carbonate) solution, and the excess of permanganate then titrated. This gives the formic acid and lactic acid together. Another portion of the extract is oxidised with permanganate, and the oxalic acid resulting from the oxidation of the lactic acid is precipitated as calcium oxalate and estimated volumetrically. Acetic acid is estimated by extracting a third portion with ether, diluting the extracted acid to 100 c.c., and distilling the solution until 95 c.c. of distillate have been collected; under these conditions, the distillate will contain 84·49% of the acetic acid. [See, further, *J. Soc. Chem. Ind.*, 715A.] W. P. S.

**New Method for the Accurate Estimation of the Content of Fatty Acids in Soaps.** E. BOSSHARD and F. COMTE (*Helv. Chim. Acta*, 1918, **1**, 251—270).—Errors are introduced in the estimation of the fatty acids in soaps when these are weighed as such, owing partly to the oxidation of the unsaturated acids and partly to the volatility of the lower fatty acids. The authors describe a method in which the acids are weighed in the form of the lead salts. An ethereal solution of the acids is evaporated in contact with lead oxide, the increase in weight thus representing the weight of the acid anhydrides. [See *J. Soc. Chem. Ind.*, 707A.] C. S.

**Biochemical Colour Tests. I. Thiophen Test for Lactic Acid. A Colour Test for Aldehydes.** WILLIAM ROBERT FEARON (*Biochem. J.*, 1918, **12**, 179—183).—The thiophen reaction for lactic acid is due to the production of formaldehyde and, chiefly, acetaldehyde from the lactic acid, which interact with the thiophen in the presence of excess of sulphuric acid to give the cherry-red colour. Acetaldehyde is much less stable in dilute than in strong sulphuric acid, and consequently if there is more than a trace of water present at the outset, the acetaldehyde will be destroyed as it is produced, and the thiophen will give no coloration.

The following general test is described for the detection of aldehydes. A couple of drops of a 0·2% alcoholic solution of thiophen are added to 5 c.c. of concentrated sulphuric acid (free from nitrites and nitrates) and mixed. On adding a drop of a weak solution of an aldehyde, a red colour develops and spreads through the acid. The test is sufficiently delicate to detect 1 part of formaldehyde in 100,000. The colour varies slightly with different aldehydes; substituted aldehydes, such as chloral, *p*-hydroxybenzaldehyde, etc., also give the test. The colours produced by this test are all discharged by a few drops of water, but are reproduced on the addition of more sulphuric acid. The author suggests the term "hydrocnic" to describe this and similar tests in which the colour produced is unstable towards water.

On the addition of phosphoric oxide to a mixture of thiophen and acetaldehyde in light petroleum, interaction occurs, and one of the products is an orange *liquid*, b. p. 121° (decomp.), which may be dithienylmethylmethane, $CH_3{\cdot}CH(C_4H_3S)_2$. H. W. B.

**Crismer Test for the Detection of Foreign Fat in Butter, Lard, etc.** ALAN W. STEWART (*J. State Med.*, 1918, **26**, 312—315).—The following modification of Crismer's test (A., 1896, ii, 506) gives values for different fats which appear to be sufficiently distinctive to render the application of the test of value for the detection of adulteration in butter, lard, etc. Three c.c. each of filtered fat and absolute alcohol are pipetted into a test-tube and heated over a small flame until the mixture, which is continuously stirred with a thermometer, has become clear. The tube is then removed from the flame, and the contents stirred until turbidity reappears. The temperature at which this occurs constitutes the Crismer number. Butter-fat gives a result varying from 50·5 to 57, whilst margarine has a value above 65 if it is composed of animal fat and under 50 if prepared from vegetable fat. The fat must be free from moisture and quite clear, and can generally be so obtained by filtration through a dried filter-paper at 100°. The Crismer values of other fats and oils are as follows: lard, 76 to 77; sesame oil, 67·5; almond oil, 64; cotton-seed oil, 61·5; arachis oil, 57·5; olive oil, 56; cocoa butter, 47; tallow, 34·5; palm oil, 22; cocoanut oil, 15 to 19·5; palm kernel oil, 13·5. Rape oil is insoluble at the boiling point of the mixture with alcohol.

H. W. B.

**New Method of Estimating Phosphatides.** C. CIACCIO (*Arch. farm. sper. sci. aff.*, 1917, **24**, 231—234; from *Physiol. Abstr.*, 1918, **3**, 309).—The methods of estimation are given in full, and from the results the "phosphatide index," which is the ratio of fatty acids to lipoid phosphorus, is calculated. The index is lessened in certain pathological states, indicating partial cleavage of the lipoids.

H. W. B.

**The Use of Benzaldehyde Sulphite Compounds as a Standard in the Quantitative Separation and Estimation of Benzaldehyde and Benzoic Acid.** G. A. GEIGER (*J. Amer. Chem. Soc.*, 1918, **40**, 1453—1456).—The work was originally commenced with a view to the analysis of toluenes chlorinated in the side-chain based on an estimation of benzaldehyde and benzoic acid. The procedure is quite accurate and useful for control analyses, but inferior in point of speed and ease of manipulation to the method of Lubs and Clark (this vol., ii, 460). In the preliminary work, benzaldehyde was found to be unsuitable as a standard, as it is too readily oxidised, but the bisulphite compound, $PhCHO,NaHSO_3,\frac{1}{2}H_2O$, fulfils the required conditions.

The estimation is carried out as follows. Solutions containing as a maximum 0·5 gram of benzaldehyde and benzoic acid are made distinctly alkaline with sodium hydroxide and extracted with three portions of ether (each 25 c.c.); the combined ethereal extracts are treated with freshly distilled phenylhydrazine (1·5 gram) and 10 c.c. of a solution of acetic acid in ether (10%). The solution is evaporated in a current of air, the residue mixed with water (50 c.c.), and the insoluble benzylidenephenylhydrazone collected in a tared Gooch crucible, dried for two hours at 70° in a vacuum, and weighed.

The solution from which the benzaldehyde has been extracted is rendered slightly acid with hydrochloric acid (1:3), extracted with chloroform (25 c.c.), saturated with salt, and three times extracted with chloroform (25 c.c. for each extraction). The chloroform is removed at the ordinary temperature, and the residue dissolved in neutral 50% alcohol and titrated with sodium hydroxide.

If the ethereal solution of benzaldehyde is washed with 25 c.c. of 0·2*N*-sodium hydroxide, the quantity of benzoic acid separated is larger and the accuracy of the method is increased. H. W.

**Estimation of Acetone in Smokeless Powders.** A. PIERONI (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 52—57).—A method is described by means of which the losses attending the conversion of acetone into iodoform and the estimation of the latter are avoided. [See *J. Soc. Chem. Ind.*, 749A.] T. H. P.

**Estimation of Acetone in Urine.** SABEL (*Rep. pharm.; Giorn. farm. chim.*, 1917, **66**, 27; from *Physiol. Abstr.*, 1918, **3**, 327).—Tartaric acid is added to 200 c.c. of urine, which are then subjected to distillation. To 50 c.c. of the distillate, a solution of iodine in potassium iodide is added, and then a slight excess of potassium hydroxide. The precipitated methyl iodide is washed with water and then heated under a reflux condenser with fuming nitric acid and silver nitrate. The silver iodide thus formed is washed, dried, and weighed. The weight multiplied by 0·1171 gives the amount of acetone. H. W. B.

**New Volumetric Method for the Estimation of Uric Acid in Blood.** L. J. CURTMAN and A. LEHRMANN (*J. Biol. Chem.*, 1918, **36**, 157—170).—The proteins in the blood are coagulated by heat in the presence of dilute acetic acid, and, after filtration, the uric acid in the filtrate is precipitated by the addition of nickel acetate in the presence of sodium carbonate. The uric acid in the precipitate is subsequently estimated by adding an excess of standard iodine solution and titrating the excess with thiosulphate solution, using starch as indicator. H. W. B.

**Estimation of the Purine Bases in Nucleic Acids after Cleavage without the Production of Humin.** R. FEULGEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 244—251).—The nucleic acid is heated with a solution of sodium hydrogen sulphite at 160° under pressure, whereby a colourless, humin-free hydrolysate is obtained. On cooling, the guanine separates quantitatively, whilst the adenine in the filtrate is precipitated as phosphotungstate, then converted into the silver sulphate compound, and finally weighed as picrate. H. W. B.

**Identification of Purine Bases in Drugs.** O. TUNMANN (*Pharm. Post.*, 1918, **51**, 305—306; from *Chem. Zentr.*, 1918, ii, 219—220).—Of the three known processes, sublimation on an asbestos plate and detection with gold chloride (if concentrated hydrochloric acid and gold chloride solution [3%] are added) yield trustworthy results; the benzene process is less satisfactory. A new method, in no way inferior to the gold chloride process, depends on the use of ammonia and chloroform. The section or powder is moistened with ammonia (this causes a strong green coloration with raw coffee), covered, treated with chloroform, and the liquids are mixed by inclining the slip. Separation of crystalline purine bases occurs within a few seconds with coffee, kola, and tea, more slowly with theobroma, and still more slowly (after about five minutes) with *Paullinia cupana.* The colourless needles either lie singly or are grouped in bundles.

Sublimation does not affect the free purine bases only, but the combined bases are also decomposed and the purine sublimes.

The ammonia-chloroform process only permits an approximate localisation of the bases. H. W.

**Application of Microchemical Methods to the Investigation of Drugs. III. Acetoanilide, Acetphenetidide, Antipyrine, Amidopyrine (Pyramidone).** ADOLF MAYRHOFER (*Zeitsch. Allg. Österr. Apoth. Ver.*, 1918, **56**, 39—41, 47—48, 57—60; from *Chem. Zentr.*, 1918, i, 1196—1197).—The microchemical recognition of acetanilide, phenacetin, and antipyrine has been described recently by Tunmann (A., 1917, ii, 551). Acetanilide may be detected by the melting point, crystalline form of aniline sulphate, and recognition of the acetyl group by ferric chloride. Identification of acetophenetidide depends chiefly on the reaction with nitric acid, the m. p., the crystalline form, and the sublimation. Antipyrine may be identified by m. p., sublimation, the *iso*nitrosoantipyrine reaction, the ferripyrine reaction, and by Wasicky's method with *p*-dimethylaminobenzaldehyde (this method is suitable for the detection of antipyrine as an impurity in other drugs); the latter test is conveniently performed by warming antipyrine with *p*-dimethylaminobenzaldehyde, when a deep yellow solution is formed, which becomes red after addition of a drop of water.

Pyramidone sublimes undecomposed slightly above its melting point, generally in droplets, which become crystalline when rubbed; the crystals appear as rectangular or quadratic plates or as rectangular needles generally united in clusters or twin crystals. The mercury double salt crystallises in needles or quadratic plates; it separates from alcohol in needles grouped in rosettes, to which slender, dendritic, crystalline threads are frequently attached. The potassium iodide-iodine reaction is much more sensitive; the yellow crystals obtained in dilute sulphuric acid solution dissolve when warmed and separate again on cooling as yellowish-brown, rectangular needles, sometimes pointed, frequently united to form aggregates. The reactions with hydriodic acid, zinc chloroiodide, and potassium mercury iodide are also very sensitive. Silicotungstic acid, after vigorous boiling in hydrochloric acid solution, yields regular, six-sided, almost colourless crystals; with antipyrine it gives only droplets, and does not react with acetanilide or phenacetin. Picric acid causes the separation of groups of yellow needles from a solution of pyramidone in hydrochloric acid.

H. W.

**Volumetric Estimation of Histidine and other Glyoxaline Derivatives.** C. L. LAUTENSCHLÄGER (*Zeitsch. physiol. Chem.*, 1918, **102**, 226—243).—Histidine can be estimated quantitatively by treating its solution with an excess of diazobenzenesulphonic acid, boiling with alcohol to destroy the excess of the acid, and then titrating the stable histidine dye with titanium trichloride by Knecht and Hibbert's method (A., 1903, ii, 509). An alternative method consists in adding standard silver nitrate to the histidine solution until a drop no longer gives a red coloration with an alkaline solution of diazobenzenesulphonic acid. As only the free base reacts with the diazo-acid to form a red dye, whilst the silver salt gives no colour reaction, the end-point is revealed by the non-appearance of the red coloration.

For its estimation in protein, the histidine must first be separated from the other products of hydrolysis, especially tyrosine, and this can be effected by means of silver lactate or mercuric chloride, which form insoluble compounds with histidine. H. W. B.

**The Berberine Nitrate Test with Hydrastis Powder.** OTTO ESS (*Schweiz. Apoth. Zeit.*, **56**, 104—105; from *Chem. Zentr.*, 1918, ii, 226).—The microchemical detection of berberine in hydrastis powder is best effected in the following manner: the powder is rubbed with a drop of alcohol and treated with two drops of nitric acid (30%); after a short time, yellow needles of berberine nitrate, up to 60 $\mu$ in length, and generally united in clusters, separate. The needles disappear when warmed, and the solution becomes red. H. W.

**Differentiation between Egg-albumin and Pathological Albuminoids.** C. PAGEL (*Bull. Sci. Pharmacol.*, 1918, **25**, 117—118; from *Chem. Zentr.*, 1918, ii, 76).—The following methods are considered trustworthy: (1) Salkowski's reaction. Nitric acid (D 1·2) is added drop by drop to the cold urine until a permanent turbidity or precipitate is obtained, followed by an equal volume of alcohol (95%); in the presence of urine-albumin, complete solution occurs, whilst with egg-albumin the turbidity is increased or a precipitate formed; in the course of twelve to twenty-four hours a considerable evolution of gas occurs in certain circumstances. (2) The urine is shaken with an equal volume of a mixture of ether (4 parts) and alcohol (95%, 1 part); in the presence of urine-albumin, a thin skin is at most formed between the layers, whilst with egg-albumin a thick layer filled with bubbles of air, which only slowly subsides, is produced; the aqueous-alcoholic layer is cloudy and yields a precipitate within twenty-four hours. (3) A mixture of urine (10 c.c.) and alcohol (95%, 100 c.c.) is filtered after half an hour, and the filter-paper is pierced; urine-albumins dissolve in a few c.c. of water, whereas egg-albumin in quantities above 2 grams per litre remains undissolved. H. W.

**Detection of Egg-albumin in Urine.** C. Barbe (*Bull. Sci. Pharmacol.*, 1918, **25**, 118—121; from *Chem. Zentr.*, 1918, ii, 75).—Three to four c.c. of a mixture of 30 c.c. of ammoniacal copper oxide solution (prepared by repeatedly pouring 100 c.c. of officinal ammonia solution over about 1 gram of copper) diluted with acetic acid to 100 c.c. are cautiously introduced beneath 3—4 c.c. of clear, fresh urine in a test-tube. In the presence of egg-albumin, a more or less transparent, sharply defined ring is formed at the junction of the layers; with quantities of less than 0·10 gram per litre, reaction occurs within three minutes. H. W.

**The Simulation of Albuminuria (Detection of Egg-albumin).** Ed. Justin-Mueller (*J. Pharm. Chim.*, 1918, [vii], **18**, 201—204).—For the rapid and exact detection of egg-albumin in urine, a slight modification of Maurel's reagent is advised. The new reagent is prepared by mixing together 25 c.c. of 33% aqueous sodium hydroxide, 5 c.c. of 10% copper sulphate solution, and 70 c.c. of glacial acetic acid. With this reagent, a ring is formed at the surface of contact of the two liquids in 30 seconds, as compared with 75 seconds with Maurel's reagent, 150 seconds if the copper sulphate is not added, and 1200 seconds with acetic acid alone. W. G.

**Preparation of Teichmann's Hæmin Crystals.** N. Bokarius (*Vierteljschr. ger. Med. öffentl. Sanitätswesen*, 1918, [iii], **55**, 255—259; from *Chem. Zentr.*, 1918, ii, 121—122).—The most suitable reagent is a mixture of acetic acid (100%, 3 parts) and saturated common salt solution (0·3 part). The suspected stains are moistened with three or four drops of the reagent, and the liquid is pressed on to an object-glass; the preparation is covered and evaporated or boiled. Alternatively, a small quantity of the suspected substance is scraped on to an object-glass and moistened with three or four drops of the reagent, the subsequent procedure being the same as that described above. Special precautions need not be observed during the heating. H. W.

**Analyses of Blood-gases. I. Qualitative and Quantitative Detection of Acids in Small Quantities of Blood by Estimation and Distribution Equilibria.** H. Straub and Klothilde Meier (*Biochem. Zeitsch.*, 1918, **89**, 156—177).—The laws of mass action regulate the relationship between (*a*) the undissociated, (*b*) the dissociated parts of electrolytes in the blood, and (*c*) the hydrion concentration. If two of these are known, the third can be calculated. A method is described for determining whether acids stronger or near the strength of carbon dioxide are present which depends on the solubility of carbon dioxide in blood or serum. It consists in the determination of the equilibria of distribution between carbon dioxide and the non-volatile acids of the blood. The determination of the absolute solubility of carbon dioxide at a given partial pressure of the gas, or at a given hydrion concentration, gives a means of estimating the amount of pathological acids present in blood. Various examples of the use of the method are given. S. B. S.

**Estimation and Meaning of Ferments in Gastric Juice.** L. MICHAELIS (*Deutsch. med. Woch.*, 1918, **44**, 685—689; from *Chem. Zentr.*, 1918, ii, 288—289).—The communication deals with rennet and pepsin. In the estimation of the former, the action of gastric juice on milk is compared with that of a standard solution of rennet prepared from a known, stable rennet preparation, such as Merck's rennet tablets. The interpretation of varying concentrations of rennet and hydrochloric acid in the gastric juice is discussed.

The estimation of pepsin depends on the fact that certain solutions of albumin which become cloudy on addition of sulphosalicylic acid are smoothly fermented by pepsin in the presence of this acid; all other precipitants of albumins destroy the action of pepsin. For the estimation, as in that of rennet, a control ferment is required; a stable pepsin solution is used for this purpose, which is standardised by comparison with a series of normal gastric juices containing, as a mean, fifteen pepsin units. The albumin solution is best prepared from a strongly albuminous urine, which is preserved by chloroform, and so diluted that it contains about 0·5% of albumin. Sulphosalicylic acid (10%) is added to this until the solution is just distinctly acid to Congo-paper, but only gives a faint violet colour. After remaining for a few minutes in a test-tube, the solution should show a just non-translucent turbidity. All the solutions must have the same hydrogen-ion concentration, which is attained in practice by using an excess of the albumin–acid solution in comparison with the amount of gastric juice, so that the influence of the latter on the action of the mixture is negligible. For the estimation, six tubes are charged with 1 c.c. of gastric juice, the latter being used pure and in dilutions of 1/2, 1/4, 1/8, 1/16, and 1/32 respectively. A control tube containing 1 c.c. of pepsin solution (1 pepsin unit) is also used. Five c.c. of albumin–acid solution are added to each tube, and the series is placed in a thermostat at 37°. After about ten minutes, a certain degree of clarification is observed in the control tube, and the solutions in the other tubes are now compared with it.

The detailed experiments show a certain parallelism between acidity, rennet, and pepsin; the relationship is only approximate, however. H. W.

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# ERRATA.

## Vol. LXXXII (Abstr., 1902).

### Part I.

| Page | Line | |
|---|---|---|
| 174 | 22 | and throughout the abstract, *for* "tropic" *read* "tropinic." |

### Part II (Index).

| Page | Line | | |
|---|---|---|---|
| 743 | 7* | col. i. | *for* "tropic acids," *read* "tropinic acids." |
| 1032 | 27 | ,, i. | |

## Vol. XCIV (Abstr., 1908).

| Page | Line | |
|---|---|---|
| ii. 395 | 22* | *for* "$C_{15}H_{20}O_6Ag$" *read* "$C_{15}H_{20}O_6Ag_2$." |

## Vol. C (Abstr., 1911).

| Page | Line | |
|---|---|---|
| ii. 406 | 18 | *for* "durites" *read* "dunites." |
| ii. 1105 | 7* | ,, "1910, A., ii, 57" *read* "1910, A., ii, 46." |

## Vol. CII (Abstr., 1912).

| Page | Line | |
|---|---|---|
| ii. 57 | 19 | *for* "idiocrase" *read* "idocrase." |
| ii. 173 | 2 | ,, "rhodocrosite" *read* "rhodochrosite." |
| ii. 357 | 14 | ,, "sopal" *read* "opal"? |

## Vol. CIV (Abstr., 1913).

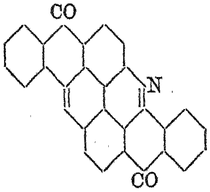
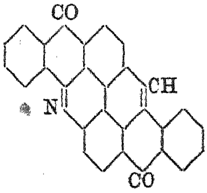
| Page | Line | |
|---|---|---|
| ii. 419 | 14 | *for* "Rev. . . ." *read* "Riv. Min. Crist. Ital." |
| ii. 419 | 20* | ,, "samseyite" *read* "semseyite." |
| ii. 423 | 3 | ,, "hornblende" *read* "hornfels." |
| ii. 423 | 7 | ,, "double refraction (mean value 1·67)" *read* "mean index of refraction 1·67." |

## Vol. CXII (Abstr., 1917).

| Page | Line | |
|---|---|---|
| i. 660 | 22* | *for* "**Bixins**" *read* "**Bixin. IV.**" |
| i. 660 | 21* | ,, "425" *read* "495." |
| i. 683 | 7* | ,, "**89**" *read* "**39.**" |
| ii. 112 | 7 | ,, "nitrate" *read* "nitrite." |
| ii. 457 | 2 | ,, "Genossen" *read* "collaborators." |
| ii. 496 | 18* | ,, "hedenbergit" *read* "hedenbergite." |

## Vol. CXIV. (Abstr., 1918).

| Page | Line | |
|---|---|---|
| i. 275 | 15 | *for* "FRIDRICIA" *read* "FRIDERICIA." |
| i. 282 | 25 | ,, "GALBRANSEN" *read* "GULBRANSEN." |

i. 307 10 ,, "  " *read* "  "

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* From bottom.

## ERRATA (*continued*).

| Page | Line | |
|---|---|---|
| i. 342 | 15* | *for* "*p*-**Aminophenol**" *read* "**Nitrobenzene.**" |
| i. 343 | 25 | ,, "benzoyl" *read* "benzyl." |
| ii. 17 | 9 | ,, "Wengel" *read* "Wenzel." |
| ii. 21 | 6* | *Insert* "[Compare, however, Fenton, Trans., 1894, **65**, 899]." |
| ii. 63 | 15* | *for* "flame" *read* "plane." |
| ii. 69 | 4 | *after* "2 : 4-dinitrotoluene" *insert* "the system." |
| ii. 69 | 4* | *for* "molecudes" *read* "molecules." |
| ii. 95 | 8 | ,, "ZACHS" *read* "LACHS." |
| ii. 102 | 15*<br>14* | *delete* "[See *Ind.*, 71A]." |
| ii. 120 | 4* | *for* "$2CaO, VO_3, 3CO_2, 10H_2O$" *read* "$2CaO, VO_2, 4CO_2, 10H_2O$." |
| ii. 323 | 10 | ,, "**Sulpharsenate**" *read* "**Sulpharsenite.**" |
| | 15 | ,, "5%" *read* "25%." |
| ii. 326 | 12* | ,, "**Vasca**" *read* "**Vaca.**" |
| ii. 372 | 23 | ,, "Tancey" *read* "Yancey." |
| ii. 470 | 10 | col. ii. *for* "i, 279" *read* "ii, 279." |

### COLLECTIVE INDEX, 1893—1902 (AUTHORS)

| Page | Col. | Line | |
|---|---|---|---|
| 218 | i | 18* | *for* "tropic acids," *read* "tropinic acids." |
| 1641 | ii | 3 & 4 | *delete.* |
| 1642 | i | 23* | *insert* "**Tropinic Acids** (GADAMER) 1902, A., i, 174." |

### COLLECTIVE INDEX, 1903—1912 (AUTHORS).

| Page | Col. | Line | |
|---|---|---|---|
| 886 | i | 22 | for "*Butea fundosa*" read "*Butea frondosa*." |
| 1012 | i | 9* | *for* "1904, A., i, 24" *read* "1904, A., ii, 39." |

### SUBJECTS.

| Page | Col. | Line | |
|---|---|---|---|
| 278 | i | 20 | *for* "A., ii, 868" *read* "A., i, 868." |
| 1317 | ii | 23* and 24* | should be deleted. |
| 1326 | ii | 30* | below this line *insert* "**3-Methoxy-4-toluic acid**, methyl ester" (GUILLAUMIN), 1910, A., i, 375. |

### NOTE TO T., 1917, **111**, 664–665.

The word "pure" in this section is intended to convey that the zinc sulphide in question was free from any intentional impurities, and that, so far as could be provided, it was also free from quantities of impurity detectable by ordinary chemical methods. It was not intended to suggest that the sulphide was spectroscopically pure. The methods of preparation described in the section obviously cannot provide against the contamination of the product with traces of zinc oxide.

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* From bottom.

# INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

# NOMENCLATURE AND SYSTEM OF NOTATION

## ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.

2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.

3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.

4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.

5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.

6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.

7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.

8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.

9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

## Nomenclature.

10. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

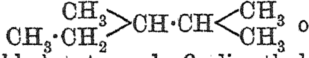
11. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulae.*

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; $CO_2$, carbon dioxide; $P_4O_{10}$, phosphoric oxide; $As_4O_6$, arsenious oxide; $Fe_2O_3$, ferric oxide.

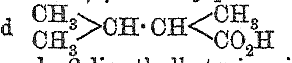
14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter *α* being assigned to the first carbon atom in the formula, except in the case of CN and $CO_2H$, for example, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2I$ *α*-iodobutane, $CH_3\cdot CH_2\cdot CH_2\cdot CN$ *α*-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,



$$\begin{matrix}CH_3\\CH_3\cdot CH_2\end{matrix}>CH\cdot CH<\begin{matrix}CH_3\\CH_3\end{matrix}$$

or $CH_3\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_3$ should be termed *βγ*-dimethylpentane not methylethyl*iso*propylmethane, and



$$\begin{matrix}CH_3\\CH_3\end{matrix}>CH\cdot CH<\begin{matrix}CH_3\\CO_2H\end{matrix}$$

or $CH_3\cdot CHMe\cdot CHMe\cdot CO_2H$ should be termed *αβ*-dimethylbutyric acid, not *αββ*-trimethylpropionic, or *α*-methyl*iso*valeric, or methyl*iso*propylacetic acid.

16. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the $C_nH_{2n+2}$ series of the form $CH_3\cdot[CH_2]_5\cdot CH_3$, &c. Term the hydrocarbons $C_2H_4$ and $C_2H_2$ ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2:C:CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus $\alpha$-ethoxypropionic acid, $OEt\cdot CHMe\cdot CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3\cdot CO_2H$, instead of diethylprotocatechuic acid; and $\alpha$-acetoxypropionic acid, $OAc\cdot CHMe\cdot CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $C_6HEt_2(OH)_2\cdot CO_2H$, and not $C_6H_3(OEt)_2\cdot CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2\cdot CO_2H$.

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups $NH_2$, NHR, $NR_2$, NH or NR, its name should end in *ino*; for example, $\beta$-aminopropionic acid, $NH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, $\beta$-anilino-acrylic acid, $NHPh\cdot CH:CH\cdot CO_2H$, $\alpha$-iminopropionic acid, $NH:CMe\cdot CO_2H$.

22. Compounds of the radicle $SO_3H$ should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 4th decade (1903–1912) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

## Notation.

25. In empirical formulae the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulae should be shortened by the judicious employment of the symbols Me for $CH_3$, Et for $C_2H_5$, $Pr^{\alpha}$ for $CH_2{\cdot}CH_2{\cdot}CH_3$, $Pr^{\beta}$ for $CH(CH_3)_2$, Ph for $C_6H_5$, Py for $C_5H_4N$, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$.

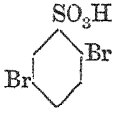
(c) That formulae should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

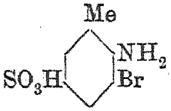
(a) The abbreviations *o-*, *m-*, and *p-*, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—

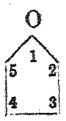


is 2 : 5-dibromobenzenesulphonic acid;

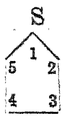


is 3-bromo-*o*-toluidine-5 sulphonic acid.

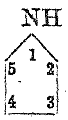
29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulae should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, of which the following schemes may be regarded as typical :—



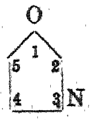
Furan.



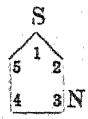
Thiophen.



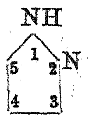
Pyrrole.



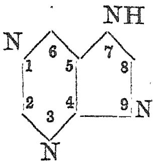
Oxazole.



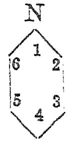
Thiazole.



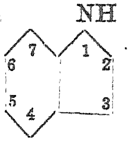
Pyrazole.



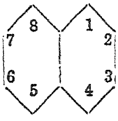
Purine.[*]



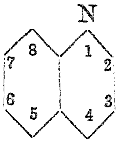
Pyridine.



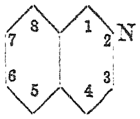
Indole.



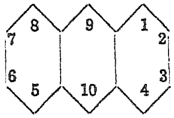
Naphthalene.



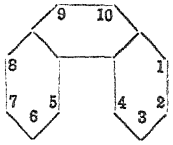
Quinoline.



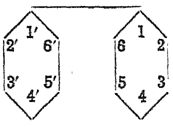
*iso*Quinoline.



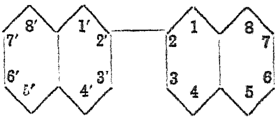
Anthracene.



Phenanthrene.



Diphenyl.



ββ-Dinaphthyl.

### Manuscript.

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

### Proofs.

34. Abstractors are expected to read and correct proofs carefully, and to check all formulae and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

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⁂ **The Editor's decision, in all matters connected with the Abstracts, must be considered final.**

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[*] This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon.*

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